CONSTITUTION
OF
THE ELECTROCHEMICAL SOCIETY, INC.

Article I

Name and Object

Section 1. The name of this organization shall be The Electrochemical Society, Inc.

Section 2. Its object shall be the advancement of the theory and practice of Electrochemistry, Electrometallurgy, Electrothermics, Electronics and allied subjects. Among the means to this end shall be the holding of meetings for the reading and discussion of professional and scientific papers on these subjects, the publication of such papers, discussions and communications as may seem expedient, and cooperation with chemical, electrical and other scientific and technical societies.

Article II

Membership

Section 1. The membership shall consist of active members, sustaining members and honorary members.

Section 2. The only requirement for eligibility to nomination as a member is that the candidate be interested in the subject of electrochemistry or allied subjects.

Section 3. Sustaining members shall be those who, through their interest in electrochemistry, contribute toward the support and development of the Society.

Section 4. Honorary members shall be those who, by reason of valuable contributions to electrochemistry, deserve special recognition by the Society.

Article III

Admission and Dismissal of Members

Section 1. Those who have, prior to April 6, 1902, notified the proper authorities that they wish to become members of the Society, are by the adoption of this Constitution elected as charter members. They shall not be required to pay an entrance fee; they shall, however, be required to pay their dues for the current year within three months.

Section 2. Application for admission after April 6, 1902, shall be made in writing in a form prescribed by the Board of Directors, and shall refer to at least two members. If the applicant is unable to do this he shall refer to at least three persons, including their addresses, of reputable standing, preferably electrochemists, chemists, electrical engineers, professors or instructors in institutions of learning. The application shall also state the present occupation of the applicant, and briefly in what capacity he is interested in the subject of electrochemistry.

Section 3. The Assistant Secretary shall submit to each Director the names and addresses of applicants and of their respective references, provided the applications are in due form. The election to membership shall be by vote of the Board of Directors or of its Executive Committee. If a candidate receives one negative vote his application shall then be considered and voted upon at a duly called meeting of the Board of Directors. Two negative votes cast at this meeting shall exclude a candidate. The Board of Directors may refuse to elect a candidate who, in its opinion, is not qualified for membership. The names of those elected shall be announced to the Society. A candidate who has been duly elected shall be placed on the rolls and have all the rights and privileges of a member as soon as his entrance fee and dues for the current year have been paid.

Section 4. A member desiring to resign shall send a written communication to the Secretary, who shall report it to the Board of Directors who may accept and announce the resignation provided the dues and other indebtedness of that member have been paid up to the time of mailing of his resignation.

Section 5. Upon the written request of ten or more active members that, for cause stated therein, a member be dismissed, the Board of Directors shall consider

the matter and, if there appears to be sufficient reason, shall advise the accused of the charges against him. He shall then have the right to present a written defense, and to appear in person before a meeting of the Board of Directors, of which meeting he shall receive notice at least twenty days in advance. Not less than two months after such meeting, the Board of Directors shall finally consider the case and, if in the opinion of the majority of the Board of Directors a satisfactory defense has not been made, and the accused member has not in the meantime tendered his resignation, he shall be dismissed from the Society.

SECTION 6. Sustaining members shall be admitted upon the approval of the Board of Directors.

SECTION 7. Honorary members shall be recommended over the signatures of at least ten members, and shall be elected only at the meeting of the Board of Directors in conjunction with a general meeting of the Society, and by the unanimous vote of the Directors, a quorum being present.

Honorary members shall pay no entrance fee or annual dues, and shall receive all the publications of the Society.

The number of honorary members shall not at any time exceed ten, and not more than two shall be elected in any one calendar year.

Article IV

DUES

SECTION 1. The entrance fee shall be payable on notification of election. If not paid within three months after notification, the election of the applicant is thereby canceled. Applicants for membership who are at the date of their election students in attendance at colleges, universities and technical institutions, shall be exempt from payment of the entrance fee.

SECTION 2. The annual dues shall be payable at the beginning of the calendar year, and notice thereof shall be mailed to each member before the end of the preceding year. If not paid before the first day of April, the delinquent member shall lose his right to vote or to receive the publications of the Society, until said dues are paid. Members will pay dues for, and receive the publications of, the year in which they are elected, but if elected after July first will pay one-half the yearly dues and receive one-half of the publications of that year. Those members elected within two months of the end of the calendar year may, at their option, pay for, and enter with, the next coming year.

SECTION 3. Any member who, at the first day of April, is in arrears for one year shall be dropped from the rolls, and shall not be included in subsequently published lists of members. The Board of Directors may reinstate a member who has been dropped, provided all his arrears have been paid.

SECTION 4. Entrance fee, annual dues and any other payments made by members to the Society shall be as prescribed in the By-Laws.

Article V

OFFICERS

SECTION 1. The officers of the Society shall be a President, three Vice-Presidents, a Secretary, and a Treasurer, who shall hold office as follows:

SECTION 2. The President, for one year. All other officers, for three years. At each annual meeting a President and one Vice-President shall be elected. At triennial periods beginning with the annual meeting of 1949 a Secretary and Treasurer shall be elected. The terms of office of the several officers shall begin at the close of the annual meeting at which they are elected and each officer shall hold office until his successor has qualified.

SECTION 3. A vacancy in the office of President shall be filled by the senior Vice-President. All other vacancies shall be filled by the Board of Directors.

SECTION 4. No officer shall receive, directly or indirectly, any salary, compensation or emolument from the Society, either as such officer or in any other capacity, or be interested, directly or indirectly, in any contract relative to the operations conducted by the Society or in any contract for furnishing supplies thereto, unless authorized either by the By-Laws or by a vote of the majority of the entire Board of Directors.

SECTION 5. No revision or amendment of this Constitution shall affect the tenure of office of any duly elected and incumbent officer.

Article VI

ELECTION OF OFFICERS

SECTION 1. Prior to October 1st each year the Board of Directors shall appoint a Nominating Committee of five members, not more than two of whom may be officers or Directors of the Society, who shall send to the Assistant Secretary prior to the next ensuing November 15th its nominations for one or more candidates for each of the offices to be filled, except that for the Vice-Presidency at least two persons shall be nominated.

In selecting the candidates for the Presidency the members of the Nominating Committee shall be limited in their choice to persons who shall have been members of the Board of Directors at some period prior to their nominations and their choice shall be confined to members who have been active in the affairs of the Society.

It shall be the duty of the Nominating Committee to notify each candidate of his selection and any candidate desiring to do so may withdraw his name within one week of such notification.

SECTION 2. At the Directors' meeting held prior to January 15th in each year, the Board of Directors shall appoint three tellers, who shall not be members of the Board of Directors, and three alternates. Should the Directors' meeting not be held, the President shall appoint these tellers, who shall be notified by the Assistant Secretary.

SECTION 3. The Assistant Secretary shall mail to every active member, on or before February 1st, a ballot containing the names of all candidates thus nominated. The voting need not be restricted to the nominees on the ballot. Voting shall be by secret letter ballot; the voter shall sign his name on an outside envelope, and the ballots shall be enclosed in an inner sealed and unmarked envelope.

Voting ballots must reach the Assistant Secretary before the first day of April. The results of the election shall be announced at the annual meeting.

SECTION 4. The tellers shall meet as soon after the first day of April as possible. The Assistant Secretary shall deliver to the tellers all ballots received, marking the outside envelopes received from members not entitled to vote because of non-payment of dues. The tellers shall open only the envelopes not thus marked, and shall proceed in secret to count the votes received before the first day of April. All ballots and unopened envolopes shall be returned to the Assistant Secretary, who shall preserve them for one month. At the end of one month the Assistant Secretary shall return to the senders all rejected envelopes and shall open all unidentified envelopes. The tellers shall prepare and sign a report of the results of the election, which shall be handed sealed to the Assistant Secretary, who shall deliver it to the presiding officer of the Board of Directors to be opened by him and reported to the Board on its first meeting after the last day of March each year. The presiding officer shall then declare to be duly elected the eligible persons receiving the greatest number of votes for the respective offices. The results of the election shall be published as soon as possible thereafter in the Society's Journal.

SECTION 5. At the request of the Board of Directors, these tellers shall count the ballots of any mail vote of the Society.

SECTION 6. The President and Vice-Presidents shall, after the expiration of the full term of office to which they were elected, be ineligible for immediate re-election to the same office. The Secretary and Treasurer may be re-elected once to the same office but neither can be elected to serve a third or subsequent term until a period of three years has elapsed since their last term in such office expired.

Article VII

MANAGEMENT

SECTION 1. The affairs of the Society shall be managed by a Board of Directors under this Constitution and By-Laws. The Board of Directors shall be composed of the President, the immediate Past President, the three (3) Vice-Presidents, the Secretary, the Treasurer, the Chairman of the Publication Committee, the Chairman

of the Membership Committee, the Chairman of the Local Section Advisory Committee, and the Chairmen of the several Divisions of the Society. The President, Vice-Presidents, Secretary, and Treasurer of the Society shall hold the same offices in this Board of Directors.

SECTION 2. The Board of Directors shall prepare and adopt a series of By-Laws which shall govern its meetings and its procedure, as also that of the Society under this Constitution. It shall require a two-thirds vote of the whole Board to adopt or amend these By-Laws; proxy and mail votes shall be counted when received before the vote is counted. The text of the proposed By-Laws or amendments shall be furnished to each member of the Board of Directors at least ten days before the meeting at which the vote on the same is to be taken.

SECTION 3. The Board of Directors may delegate any or all of its powers, except in those cases in which this Constitution requires a vote of the whole Board, to an Executive Committee of not less than five members of the Board of Directors. The President, the Secretary and the Treasurer shall be members of this Executive Committee. This committee shall conduct the affairs of the Board of Directors between its meetings. All members of the Board of Directors shall receive notice of the meetings of this Executive Committee and shall have the right to attend and vote. A majority of the Executive Committee shall constitute a quorum.

SECTION 4. At the request of the President, matters requiring action by the Board of Directors may be discussed and voted upon by mail vote of the Board of Directors.

SECTION 5. The duties of the President, Vice-Presidents and Treasurer shall be such as usually pertain to the offices they hold, besides any other designated in the Constitution or By-Laws or by the Board of Directors. The Secretary shall be in administrative charge to direct and supervise the duties usually pertaining to this office or designated in the Constitution or By-Laws or by the Board of Directors; but he shall be relieved of the clerical or other work in executing these duties by an Assistant Secretary, who shall be appointed annually by the Board of Directors and shall be responsible to the Board. The Secretary shall instruct the Assistant Secretary in his or her duties, and the work of this Assistant Secretary shall be done under the direct supervision of the Secretary. The Secretary and Assistant Secretary shall in all matters concerning the affairs of the Society carry out the prescriptions of the Constitution, By-Laws, rulings and precedents, and in cases in which no such prescriptions exist they shall obtain decisions from the Board of Directors or Executive Committee, or if time does not permit they shall confer with the President. All funds expended in the Secretarial duties shall be under the control of the Secretary, who shall be responsible to the Board of Directors for the proper dispensing of such funds. The Secretary and the Treasurer shall present reports annually to the Board of Directors before the annual meeting. The Board of Directors shall present a report annually to the Society at the annual meeting; the material for such report shall be prepared by the Assisstant Secretary under the direction of the Secretary. The nature of these reports shall be specified in the By-Laws.

SECTION 6. All standing committees shall be directly responsible to the Board of Directors, and shall be appointed by the President subject to the approval of the Board of Directors.

Article VIII

MEETINGS

SECTION 1. The annual business meeting shall be held between April 1st and July 1st, at such time and place as the Board of Directors shall designate. Business affecting the organization of the Society shall be transacted only at the annual meetings. Proxy or mail votes shall be received.

SECTION 2. Other meetings may be held at such times and places as the Board of Directors shall select. The President shall call a meeting at the written request of thirty or more active members.

SECTION 3. Notice of all ordinary meetings shall be sent to all members at least twenty days in advance, and of the annual meeting, thirty days in advance.

SECTION 4. Any ten active members at a meeting of the Society may require that any motion brought up be submitted to a referendum of the Society by a mail vote.

BY-LAWS

Article IX

General

Section 1. A quorum of the Society shall consist of fifty active members, present in person or by proxy.

Section 2. Only those members whose dues have been paid for the current fiscal year shall be entitled to vote at any meetings. A member may vote by proxy or, when the subject matter has not been changed, by mail. No proxy shall be valid after the expiration of eleven months from the date of its execution. Every proxy shall be revocable at the pleasure of the person executing it.

Section 3. The fiscal year of the Society shall begin January 1st.

Article X

Amendments

Proposals to amend this Constitution shall be made in writing to the Board of Directors and signed by at least ten active members; they shall reach the Secretary not later than February 1st. The Board of Directors shall consider them and may amend them. The original, with the action of the Board of Directors, shall then be presented to the Society at its annual business meeting, at which time it may be further amended. In its final form it is to be voted upon by a mail vote of the members of the Society which is to be taken as soon after the annual business meeting as practicable. A majority of the votes cast shall decide.

BY-LAWS

Article I

Order of Business

Section 1. At the annual business meeting of the Society the order of procedure shall be as follows:

Reading of the minutes of last meeting.

Report of the Board of Directors, including those of the Secretary and the Treasurer.

Reports of Standing Committees.

Deferred business.

New business.

Report of tellers of election.

Address of the retiring president. (This may be presented at another session of the general meeting, at the discretion of the framers of the program of the meeting.)

Section 2. The annual business meeting of the Society shall preferably be on the second day of the general meeting.

Article II

Meetings of the Board of Directors

Section 1. The Board of Directors shall hold a regular meeting immediately preceding each general meeting of the Society.

Section 2. Between said meetings the Board of Directors may hold special meetings when called by the President.

Section 3. All meetings of the Board of Directors shall be open to Past Presidents.

Section 4. At the regular meetings of the Board of Directors the order of procedure shall be as follows:

Reading of the minutes of the last regular meeting and of any special meeting the minutes of which have not been approved.

Election of new members.

Appointment of tellers of election.

Approval of bills.

Communications from the President.

Communications from the Treasurer.

Communications from the Secretary.
Discussion of programs of future meetings of the Society.
Reports of Committees.
Deferred business.
New business.
Adjournment.

SECTION 5. At special meetings of the Board of Directors, the order of procedure shall include the reading of the minutes of the past meeting of the Board and such other of the above items of procedure in their order given as are to be acted upon.

Article III

QUORUM OF DIRECTORS

A quorum of the Board of Directors shall be a majority, present in person or by proxy.

Article IV

DUTIES OF OFFICERS

SECTION 1. The President shall preside at all business meetings of the Society and at those of the Board of Directors. He may represent the Society at any function to which no other particular delegate has been appointed by the Society or the Board of Directors. The President (or any director) shall have the power of appealing any action of the Executive Committee to the Board of Directors, within two weeks of its adoption, which action can then be carried into effect only after approval by a majority of the entire Board of Directors voting on said explicit action either in person or by mail ballot. He shall deliver an address at the annual meeting of the Society at which his term of office expires.

SECTION 2. The Vice-Presidents, in the order of their seniority, shall assume the duties and responsibilities of the President in case of his death, disability or absence from fulfilling his duties.

SECTION 3. The Secretary, besides performing the usual duties of that office, shall be the guardian of the records of the Society, collect dues from members, and all bills owing to the Society, and pay such amounts to the Treasurer. He shall collect and receive manuscripts of papers, with drawings or diagrams thereto belonging, submitted for presentation at meetings of the Society and shall be responsible for their custody until he hands them to the Publication Committee. He shall report to the Board of Directors at its meeting held at the annual meeting of the Society, on the condition of the affairs of the Society, such as the membership, publications, meetings, number of papers read, and in general a summary of the work and condition of the Society, excepting its finances, and make such recommendations as he thinks will facilitate the transaction of the business affairs of the Society or in any way advance its interests. It shall be the further duty of the Secretary to organize and maintain means for securing the submission of papers to the Publication Committee.

SECTION 4. The Treasurer shall report to the Board of Directors at its meeting immediately preceding the business session of the annual meeting of the Society on the condition of the finances of the Society and make such recommendations as will in his opinion tend to safeguard or improve the same.

SECTION 5. The Board of Directors shall report to the annual meeting on the general affairs of the Society, including the abstracts of the reports of the Secretary and Treasurer and any other matters which they may consider of interest to the Society.

Article V

PUBLICATION COMMITTEE

SECTION 1. The Publication Committee shall consist of a Chairman, the President (ex officio), the Secretary (ex officio), and one member from each Division of the Society. The Division members shall be selected annually by the President subject to the approval of the Board of Directors from two members named by the

Executive Committee of each Division. The Chairman, to serve one year, shall be appointed by the incoming President subject to the approval of the Board of Directors. Retiring members shall be eligible for re-appointment. Vacancies arising on the Publication Committee shall be filled by appointment by the President subject to the approval of the Board of Directors.

SECTION 2. The Publication Committee shall meet at such times as its work may require and shall set dates prior to which papers for succeeding meetings may be submitted. It shall pass on all papers so submitted, and shall have complete discretion as to what papers shall be accepted for presentation at the meetings of the Society; provided, however, that any member may appeal to the Board of Directors against any decision of the Committee in respect to a paper submitted by that member.

The Committee shall deal with all papers submitted as promptly as possible, and shall, where desirable, assist authors by suggestions which would improve the form of their papers as submitted.

No member of the Committee shall pass on any paper of his own.

SECTION 3. The Committee shall have charge of the publication of the Transactions of the Society, and shall decide what papers shall be published in the Transactions. Inclusion of the title of a paper in a Society convention program does not necessarily imply publication in the Transactions. The editing of the Transactions shall be in the hands of the Committee.

SECTION 4. The Committee may assign work in connection with its duties to whatever member of the Society it sees fit.

SECTION 5. The Chairman of the Publication Committee shall keep a record of all papers submitted and of the action taken thereon. He shall report to the Board of Directors at each general meeting of the Society, and shall be responsible to the Board for the carrying out of the Committee's duties according to the By-Laws.

SECTION 6. In general, no paper may be presented at a meeting of the Society unless it has been submitted in full prior to a date set by the Board of Directors early enough to allow consideration by the Committee. This limiting date may, at the discretion of the Board, be extended.

SECTION 7. In exceptional cases, the President may authorize a paper, not previously submitted to the Publication Committee, to be read; such authorization will not, however, bind the Society or the Publication Committee in any way as to printing or publication.

SECTION 8. Papers of the following classes will be regarded as undesirable:

(1) Those containing too little information or obviously incorrect information.

(2) Those containing only information already easily accessible.

(3) Those of an advertising nature not counterbalanced by adequate scientific information and treatment.

SECTION 9. Authors' abstracts of papers already published elsewhere may be accepted for the purpose of discussion. Papers already published but not easily accessible will, it otherwise desirable, generally be accepted.

SECTION 10. In case of papers of a general or review nature solicited for a symposium, the Publication Committee may accept such papers which, in the opinion of the Board, are desirable for the complete treatment of the symposium subject.

SECTION 11. Concerning the question of papers dealing with analytical methods, the paper must

(1) Describe an electrochemical method of analysis or deal with analysis of a substance which enters into or is a product of an electrochemical or electrothermal process.

(2) Cover some novel method or methods or critical comparison of existing methods.

(3) Contain some actual experimental results illustrating the method.

SECTION 12. Regarding manuscripts submitted over the name of a company research staff, the name of at least one individual should be attached to the paper.

SECTION 13. The Publication Committee shall limit the number of papers for a given meeting in accordance with the number of pages allowed in the volume.

SECTION 14. No biased action shall be exercised by the Publication Committee in considering the acceptability of papers submitted by nonmembers of the Society.

SECTION 15. Foreign contributors of papers are requested and encouraged to sub-

mit their manuscripts in translated form. To prevent delays, they are urged to submit their papers as early as possible. Papers from foreign countries should reach the Society one month in advance of the closing date for the acceptance of papers for a given meeting.

SECTION 16. The final report on any manuscript is to be submitted by the Chairman of the Publication Committee to the Secretary who will advise the author or authors as to the findings and suggestions of the Committee.

SECTION 17. Papers accepted by the Publication Committee and recommended by them for publication will be so published as soon as conveniently possible in the Journal of The Electrochemical Society. The author (or joint authors) will each receive gratis five copies of his paper and will have the right to order as many reprints as he may wish at rates to be fixed by the Society.

SECTION 18. The Publication Committee will edit discussions; it shall not, however, change the meaning of any contributor's remarks, and the revised form of each contributor's remarks will be sent to him for approval; unless objection be raised within one week (allowing time for transmittal) it will be assumed that such is approved.

Article VI

PUBLICATIONS OF THE SOCIETY

SECTION 1. Effective January 1, 1948 there is established a monthly publication of the Society to be called "Journal of The Electrochemical Society."

SECTION 2. The Journal of The Electrochemical Society shall contain (a) technical articles approved by the Publication Committee for presentation at meetings and publication in the Journal; (b) such news items and other matters of general interest to the membership of the Society as may be decided upon from time to time by the Board of Directors.

SECTION 3. The Board of Directors shall appoint annually an Editor of the Journal to handle the details of its printing and publishing; and in this duty he (or she) shall be guided by an Editorial Board consisting of three members appointed annually by the Board of Directors.

SECTION 4. The technical papers appearing in the Journal, with discussions thereon which were recorded when these papers were presented at a meeting of the Society, and any other discussion submitted in writing before a closing date set by the Editorial Board shall be bound semi-annually into a volume of "Transactions of the Electrochemical Society." These Transactions shall not contain news items of passing or ephemeral value but may contain such reports and information concerning the Society's activities as may be deemed proper by the Board of Directors.

Article VII

WAYS AND MEANS COMMITTEE

SECTION 1. A Ways and Means Committee shall be established to act as an advisory group to the President and Board of Directors on all phases of the Society's business.

SECTION 2. The Ways and Means Committee shall be composed of seven members. The Chairman of this Committee shall be appointed from among the Board of Directors and it shall include at least two Past Presidents of the Society. The members of this Committee shall be appointed immediately after the annual election, by the President, subject to the approval of the Board of Directors.

SECTION 3. The Ways and Means Committee may carry on its business through subcommittees composed of a Chairman who shall always be a member of the Committee, and such other members of the Society at large as the Chairman of such subcommittee may select.

SECTION 4. The Ways and Means Committee shall have the power to call on any of the officers of the Society or of its sections or divisions to furnish this Committee with such information as it may deem necessary competently to advise the President and Board of Directors as to policies to be followed in the conduct of the Society's affairs.

SECTION 5. The Ways and Means Committee shall report at appropriate intervals

to the President and Board of Directors upon such items of the Society's business as have been referred to this Committee for attention; and on the receipt of such report the Board may take such action as it deems proper in the premises.

Article VIII

Membership Committee

Section 1. A Committee on Membership whose function shall be to enlarge by systematic effort the membership of the Society shall be appointed annually by the incoming President. It shall consist of fifteen or more members including at least one from each Division and each Section of the Society.

Section 2. Each Division of the Society shall submit annually to the President of the Society the names of two of its members and the President shall with the approval of the Board of Directors select one of the persons so proposed as that Division's representative on the Membership Committee.

Section 3. In addition to the members of the Membership Committee as provided for in this article the President shall appoint, subject to the approval of the Board of Directors, a Chairman of the Membership Committee. He shall serve for one year and may be re-appointed.

Article IX

Accounts of the Society

The Board of Directors (or its Executive Committee) shall engage a competent public accountant, not later than December 15th each year, to audit the current accounts and financial statements of the Secretary and Treasurer of the Society. The report of such accountant shall be submitted in such form as to designate the source of all receipts by the Society and the disposition of all funds expended. It shall also include as far as possible a statement of the assets and liabilities of the Society so drawn up as to show clearly the net worth of the Society as of December 31st of the year for which the audit is made.

The report of the auditor shall be sumitted to the Board of Directors through the Treasurer of the Society; and upon its receipt the Board shall take such action as may be proper with respect to such report.

This report shall be printed in the Society's Journal not later than two months after its approval by the Board, and at the Board's discretion may be bound in the then current volume of the Society's Transactions.

The general results of this audit shall always be reported to the members of the Society at the Annual Meeting.

Article X

Guests at Meetings

Guests may be invited to the meetings of the Society by members. They may be given the privilege of attending the meetings and such further privileges as the Local Committee, the President or the Secretary may extend to them.

Article XI

Session on Electrothermics

At one general meeting of the Society each year at least one session shall be devoted to the subject of Electrothermics.

Article XII

Divisions

Section 1. Professional groups, to be known as Divisions of the Society and to be organized from its members, may be authorized by the Board of Directors. Any member of the Society may register for membership in any Division in which he is interested and may resign therefrom at his discretion.

Section 2. The Officers of the Division shall be a Chairman, one or more Vice-

Chairmen, and a Secretary-Treasurer. The above officers, together with two other members of the Division, shall constitute the Executive Committee of the Division.

The Division shall elect its officers and other members of the Executive Committee during a general meeting of the Society or within thirty days thereafter. The officers and other committee members shall be elected for such terms as the Division By-Laws may provide, these terms of office not to exceed two years unless an individual should be re-elected.

SECTION 3. A Division shall have the right to make rules for its own government, subject to the approval of the Board of Directors, not inconsistent with the Constitution and By-Laws of the Society. Amendments or additions to these rules shall also be subject to the approval of the Board of Directors.

SECTION 4. A Division shall hold, if possible, one session a year at a general meeting of the Society, such session to be under the auspices of said Division, and publication of papers for such sessions to be subject to the usual regulations and control of the Publication Committee.

SECTION 5. The Society shall not be responsible for any debts contracted by the Divisions or by the officers thereof. Divisions may receive from the Society such financial assistance as the Board of Directors may determine to be proper. Such funds shall be used for sending out notices, for solicitation of papers, and for the legitimate work of the Divisions.

SECTION 6. The Board of Directors may recommend the dissolution of any Division of the Society, such recommendation to be acted on at an annual business meeting of the Society.

SECTION 7. Divisions shall have the privilege of suggesting to the Nominating Committee the names of eligible candidates for officers of the Society. Such suggestions shall be in the hands of the Nominating Committee prior to October 15th each year.

SECTION 8. It shall be the duty of the Assistant Secretary of the Society to call to the attention of the officers of each Division all of the provisions of Article XII at least once between January 1st and April 1st each year.

Article XIII

REGULATIONS CONCERNING THE FORMATION AND CONDUCT OF LOCAL SECTIONS

SECTION 1. A Local Section of this Society may be authorized by the Board of Directors, at the written request of three members. Only one Section shall be authorized in any one locality.

SECTION 2. Any member of the Society in good standing is automatically a member of a Local Section, provided that he resides or has his principal place of business within a radius of fifty miles of the city in which the Local Section has its headquarters, and provided also that he complies with the regulations of the said Section. Members of the Society who live or have their business more than fifty miles from the headquarters of the nearest Local Section may be included in the membership of such Section, provided specific request is made to the Secretary of the Society and approved by the latter. Only members of this Society are eligible to membership in its Local Sections.

SECTION 3. The regulations of Local Sections are subject to the approval of the Board of Directors.

SECTION 4. The following provisions shall apply to financial matters of common interest to the Local Section and the Society: (1) The expenses of each Local Section shall be borne by the members enrolled in said Section. The Society shall not be responsible for any debts contracted by a Local Section or by the officers thereof. Exceptions can be made only in the case of National Meetings for which the Local Section acts as host, as provided in Section 8 below.

(2) Local Sections submitting proof of at least three independent technical meetings during the fiscal year of the Society will thereupon be granted a sum of fifty dollars each as financial assistance. Additional financial assistance up to fifty cents per member may be provided by the Society in each fiscal year, provided the Local Section raises an equal amount from local dues, assessments, or transfer of funds from inactive accounts. Such additional assistance will be made only upon written request of the Local Section. Funds received by Local Sections from the Society as

provided herein shall be used solely for the rent of rooms, sending out notices, and paying legitimate expenses of persons invited to speak before such Local Sections.

(3) Local Sections will receive one dollar from the initial dues of a new member, such sum to be sent to the Local Section by the Secretary of the Society, provided the Local Section was active in securing said new members. To obtain credit for new members, the application must be forwarded to the Secretary of the Society by the Secretary of the Local Section.

SECTION 5. Papers read before Local Sections, and discussions thereon, if reported, are to be considered as the property of this Society. They shall be submitted to the Publication Committee of the Society and published in the Journal if approved by it. Reading of a paper before a Local Section does not carry with it the right of publication in the Journal.

Papers read before Local Sections may be offered for reading at general meetings of the Society, and will be given equal standing with other papers on the program of said meeting, when approved by the Publication Committee.

SECTION 6. The Board of Directors shall have the right to pass upon such questions concerning the welfare of Local Sections as are not covered by these Regulations.

SECTION 7. Each Local Section shall transmit promptly after each meeting, to the Secretary of the Society, an abstract of its proceedings, including the titles and names of authors of all papers read before it, for the purpose of preparing a report to the Board of Directors, and for the purpose of enabling the Board of Directors to comply with Sections 3 and 5 of these Regulations.

SECTION 8. When a Local Section acts as host for a National Meeting of the Society, it shall elect one of the following two plans for handling finances of such meeting and shall so advise the Secretary of the Society not less than 90 days prior to the opening of such meeting: *Plan A*—The Local Section assumes full responsibility for handling finances of the National Meeting, is responsible for all debts, and may retain any surplus, and provided further that the expenditures of any surplus retained by the Local Section shall be subject to the general approval of the Board of Directors. Local Sections shall submit a complete financial report to the Secretary of the Society within 10 days after the close of the Convention and in case of a deficit shall notify the Secretary when said deficit has been discharged. *Plan B*—The Local Section assists the Board of Directors and the Secretary of the Society in handling the finances of the National Meeting in this territory, but makes no financial arrangements without the written approval of the Secretary of the Society; the Society shall be responsible for any deficit and shall retain any surplus.

SECTION 9. Upon the request of a Local Section, the Secretary will endeavor to arrange for an outstanding speaker to visit such Section, provided the Section will accommodate its meeting date to whatever extent is necessary. The Society will be responsible for transportation costs of the speaker between cities; the Local Section will be responsible for local expenses of the speaker while he is in their city. Suggestions as to preferred speakers will be welcomed by the Secretary of the Society.

SECTION 10. Prior to July 1st each year, each section shall elect a delegate to the Local Section Advisory Committee which is hereby set up as a standing committee of the Society. Such delegate shall hold office for two years beginning on July 1st immediately following his or her election; and each section shall be entitled to two (2) such delegates.

SECTION 11. The Local Section Advisory Committee shall hold a meeting at each General Meeting of the Society. This meeting shall always precede the meeting of the Directors of the Society held at the same General Meeting. The duties of the Local Section Advisory Committee shall be: (1) to consider problems affecting the welfare and operation of the local sections and to work out their solutions; (2) to act as a clearing house on information, problems, and methods of organization of local sections; (3) to act as an Advisory Committee to the Board of Directors of the Society on Local Section affairs.

SECTION 12. Between the annual election of the Society and July 1st of the same year, the President of the Society shall appoint, subject to the approval of the Board of Directors, a Chairman for the Local Section Advisory Committee. Such Chairman shall at once, by virtue of his appointment, become a member of the Board of Directors of the Society, and shall act as the Local Section Advisory Committee's represen-

tative on the Board. He shall hold office for a term of one year, and may be reappointed for not more than three (3) years in succession.

SECTION 13. Local Sections shall have the privilege of suggesting to the Nominating Committee the names of eligible candidates for officers of the Society. Such suggestions shall be in the hands of the Nominating Committee prior to October 15th each year.

SECTION 14. It shall be the duty of the Assistant Secretary of the Society to call to the attention of the officers of each Local Section all of the provisions of Article XIII at least once between January 1st and April 1st each year.

Article XIV

DUES AND FEES

SECTION 1. The entrance fee, payable on notification of election, shall be five dollars unless waived by the Board of Directors.

SECTION 2. The annual dues shall be ten dollars of which seven dollars and fifty cents shall be a non-deductible subscription to the Journal of The Electrochemical Society. The subscription price of the Journal to non-members shall be ten dollars annually. The price of single copies of the Journal to members and to non-members shall be set annually before November 1st for the next year by the Board of Directors.

SECTION 3. The price of the current Transactions of the Society to members and to non-members shall be set annually before November 1st for the next ensuing year by the Board of Directors.

SECTION 4. Life membership in the Society, including subscription to the Journal, shall be one hundred and fifty dollars which sum shall relieve the member of future payment of annual dues. The Board of Directors shall before November 1st of each year set a price at which life members elected during the ensuing year shall pay for a life-time subscription to the Society's Transactions; provided further that such subscription rates shall not be changed for any life member after he has paid the agreed upon subscription price in full.

SECTION 5. Members who have reached the age of sixty-five and who have paid dues for thirty years shall thereafter be exempt from the payment of annual dues; they shall receive the Journal of The Electrochemical Society without charge.

SECTION 6. Any entrance fee paid by an applicant shall be returned if the applicant is not elected.

SECTION 7. Society Divisions and Local Sections may collect Division or Section dues as authorized by their respective By-Laws.

Article XV

INDUSTRIAL EXCURSIONS

Attendance at industrial excursions shall be limited to registered members of the Society and their registered guests. It shall be understood and agreed that no one shall visit the plant of a competitor in connection with the industrial excursions of the Society, except with special permission from the authorities of the plant visited.

Article XVI

AMENDMENTS

Amendments to these By-Laws may be proposed by the Board of Directors and shall require a two-thirds vote of the whole Board for their adoption; proxy and mail votes shall be counted when received before the vote is counted. The text of the proposed amendments shall be furnished to each member of the Board of Directors at least ten days before the meeting at which the vote on the same is to be taken.

LARGE-SCALE LABORATORY PRODUCTION OF DUCTILE ZIRCONIUM[1]

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ABSTRACT

On the basis of results obtained from small-scale laboratory work, equipment for the production of 60 pounds of zirconium sponge a cycle has been placed in operation.

Zirconium carbide, prepared from zircon and carbon in an electric arc furnace, is chlorinated in improved equipment capable of producing over 300 pounds a day. The raw zirconium chloride is purified in a unit which accommodates nearly 200 pounds. Reduction by magnesium is carried out in the same furnace as the purification. Excess magnesium and magnesium chloride are removed by a combination melting and vacuum distillation method. The zirconium sponge is pressed into briquets and melted in graphite crucibles in a new graphite resistor vacuum furnace capable of melting over 10 pounds of zirconium a charge.

INTRODUCTION

A previous report (1) describes the small-scale laboratory production of zirconium, while the present paper presents data on the operation of a plant capable of producing about 60 pounds of zirconium a cycle. The operation of the larger-scale unit involves the reduction of zirconium chloride vapor with magnesium in a helium atmosphere and vacuum distillation as described previously.

Zircon sand, which is used as the starting material for the production of zirconium metal, is rather widely distributed throughout the world. The production of zirconium, as developed at the Northwest Electrodevelopment Laboratory of the Bureau of Mines, U. S. Department of the Interior, Albany, Oregon, consists of the following steps:

1. Production of zirconium carbide from zircon sand
2. Chlorination of zirconium carbide
3. Purification of zirconium chloride
4. Reduction of refined zirconium chloride with magnesium metal
5. Removal of magnesium chloride (formed in the reduction phase of the process) and excess magnesium from the zirconium, by melting and fusion of the zirconium.

The various steps of the operations will be discussed under the individual headings.

PRODUCTION OF ZIRCONIUM CARBIDE FROM ZIRCON SAND

Zirconium carbide was produced by mixing zircon ($ZrO_2 \cdot SiO_2$) with carbon and fusing the mixture in an arc furnace. This operation has been

[1] Manuscript received April 6, 1948. This paper prepared for delivery at the Columbus, Ohio Meeting, April 14 to 17, 1948.

discussed previously (1). No modifications were made in procedure or capacity. Experiments have indicated that a charge containing about 18 per cent carbon, in the form of graphite, produced a grade of zirconium carbide that could be chlorinated without difficulty. The usual charge to the furnace contained about 77 per cent unground zircon sand (67 per cent zirconium oxide), 18 per cent graphite powder that had been screened through 20-mesh, and 5 per cent recirculated, incompletely reacted material from the previous operation. The resulting zirconium carbide analyzed 75.6 per cent zirconium, 5.1 per cent silicon, 1.33 per cent iron and 1.8 per cent free carbon.

CHLORINATION OF ZIRCONIUM CARBIDE

A chlorinator, consisting of a vertical shaft furnace and condenser, was constructed as shown in Fig. 1. Both the shell of the furnace [6] and the condenser [18] are made of sheet nickel, welded gas-tight. The chlorination furnace, which is 21 inches in outside diameter and 46 inches in height, is lined with silica brick [7] set in a mortar made of silica flour and sodium silicate. The internal diameter of the furnace is about 8½ inches. A conical water-cooled bottom with an iron elbow [8] is used for introducing chlorine and removing the chlorinated residue. The conical bottom, not lined with refractory, is water-cooled. A sheet nickel box or header [16] is welded on top of the main shell. This header box supports the split-graphite resistor heating-element [11] with its water-cooled clamp [15]. The products of chlorination are carried to the condenser by a sheet-nickel tube 5 inches in diameter. A heating unit [12] keeps this tube above 331°C. to prevent condensation of zirconium chloride. A charging hole [13] and thermocouple well [14] complete the arrangement of the top. The flow of chlorine from the tank [2] on the platform scales [1] is controlled by an iron needle valve [3]. An orifice flow meter [4] measures the rate of chlorine addition and the pressure gauge [5] indicates the internal pressure.

The condenser [18] is a double-walled, sheet-nickel cylinder 30 inches in diameter with about a 1-inch space between the walls. To prevent condensation of silicon chloride formed from silicon carbide in the zirconium carbide, the condenser is heated to about 100°C. by passing air from a tube [23] through a heater [22] into the space between the walls, around the baffles, and out an opening in the top [17] of the condenser. The over-all height of the condenser is 58 inches. The bottom portion of the condenser is conical and has a gas-tight trap door [24] for easy discharge of the condensed zirconium chloride into a barrel [25].

In the present intermittent operation of the chlorination equipment, about 12 inches of inert material is present in the bottom of the chlorination furnace, normally residue from the previous run. The remaining space is filled with zirconium carbide crushed to minus ¼ inch. The charge is heated by the split-graphite heater element [11] operating on 600 amperes at 8 volts. When the temperature reaches 500°C., chlorine gas is admitted at the rate of about 6 pounds an hour. Chlorine appears at the exit [20] until the heat of reaction raises the temperature to about 1,000°C. The chlorine flow is then increased to 10 to 14 pounds an hour until chlorine again appears in the exhaust gases. The power is then shut off and the equipment allowed to cool. When cool, about 45 pounds of residue is removed through

the door [9] leaving the balance of the charge in the lower part of the furnace and the cycle repeated. Experience has shown that zirconium carbide, which has been chlorinated once, may be recharged and rechlorinated with very good results. Zirconium chloride is usually removed at least once during the chlorination. It is possible that the chlorination operation could

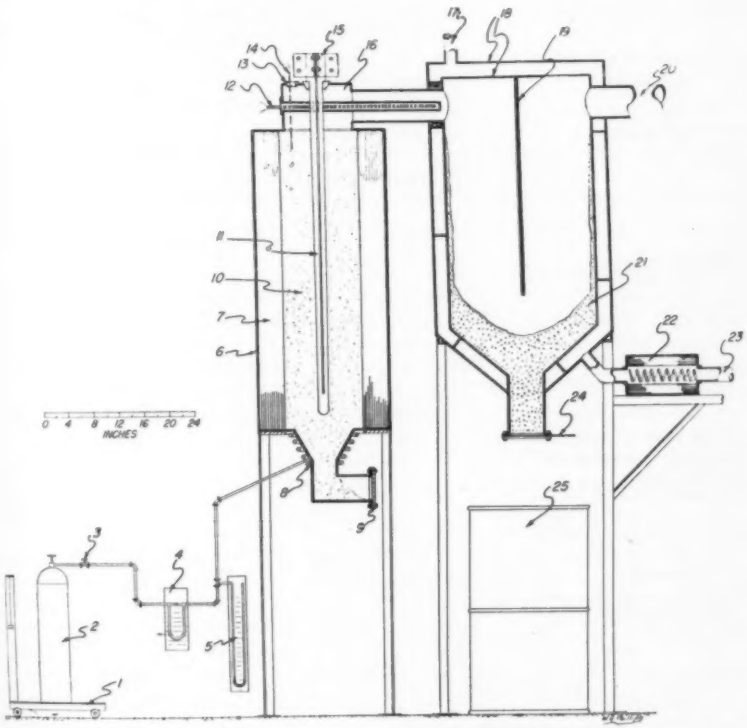

FIG. 1. Chlorinator for producing zirconium chloride

1. Platform scales 2. Chlorine tank 3. Needle valve 4. Orifice flow meter 5. Pressure gauge 6. Nickel shell 7. Silica brick lining 8. Water cooled elbow 9. Clean-out door 10. Zirconium carbide 11. Split graphite electrode 12. Heating unit 13. Feed opening cover 14. Thermocouple 15. Water cooled electrode clamp 16. Nickel elbow 17. Hot air outlet 18. Condenser 19. Baffle 20. Fume outlet 21. Zirconium chloride 22. Air heater 23. Air intake 24. Sliding gate 25. Barrel

be carried on continuously. The furnace as constructed has produced more than 300 pounds of zirconium chloride in 24 hours of operation.

After a series consisting of 5 cycles, calculations were made on the efficiency of the operation. Table I gives the results for the average cycle as calculated from the information obtained.

Examination of the residue discard indicated that it contained an appreciable quantity of unreacted zircon. Zirconium recovery could be considerably increased by returning this discard to the zirconium carbide sten for further treatment. Recoveries of about 90 per cent zirconium should be obtained by this procedure.

TABLE I. *Results obtained in average cycle from chlorination of zirconium carbide*

Time of chlorination	18 hours
Charge of new zirconium carbide	189 pounds
Chlorine used for chlorination	217 pounds
Zirconium chloride produced	280 pounds
Residue discard	46 pounds

Analysis, per cent

	Zr	Si
Zirconium carbide	75.6	5.1
Residue discard	54.6	5.8

Zirconium, chlorine, and silicon balances

Zirconium balance	Pounds	Per cent
	Zr	Zr
Charge of zirconium carbide	143	100
Recovered as zirconium chloride	110	78
Residue discard	25	17
Loss (stack, handling, etc.)	8	5
Chlorine balance	Cl_2	Cl_2
Chlorine added	217	100
Recovered as zirconium chloride	171	79
Loss as silicon chloride	34	16
Loss (stack, etc.)	12	5
Silicon balance	Si	Si
Silicon added in zirconium carbide charge	9.6	100
Removed as silicon chloride	6.9	74
Residue discard	2.7	26

Production of over four thousand pounds of zirconium chloride has been accomplished using the present equipment, and as yet no visible deterioration has occurred.

PURIFICATION OF ZIRCONIUM CHLORIDE

The zirconium chloride as obtained from the chlorination equipment is a powder of low apparent density and contains as impurities small amounts of iron and chromium as well as zirconium oxide. In the chlorination operation, any iron present in the zirconium carbide is chlorinated along with the

zirconium and eventually is found in the condenser as ferric chloride. The iron may be separated from the raw zirconium chloride by sublimating the zirconium chloride in an atmosphere of hydrogen. The ferric chloride, with a sublimation point of 315°C., is reduced by hydrogen to ferrous chloride, which has a boiling point of 1,028°C. and so remains behind. Chromium is likewise removed as chromous chloride, which has a boiling point of 1,200°C. Zirconium chloride sublimes at 331°C. and sublimes practically free from these reduced salts and zirconium oxide.

A drawing of the equipment used for making the pure dense zirconium chloride is shown in Fig. 2. It consists of a furnace [33] equipped with three separate sets of heating coils—a lower heating coil [34], a middle heating coil [35], and an upper heating coil [36] used for heating the bismuth-lead seal in annular trough [3]. The furnace is set on I-beams [38] in a pit [37] in order that the top of the furnace will be at a convenient height for the operator. A sheet-iron enclosure [31], arranged with suitable doors, connects the furnace with an exhaust duct [32] to remove any fumes that may escape during operation.

The outer reaction vessel [2] consists of a $\frac{3}{16}$ inch stainless steel shell, 20 inches in diameter and 52 inches in height. A gas-tight thermocouple protection tube [40] extends to the upper portion of the vessel. One thermocouple [39] indicates the internal temperature of the lower zone and another [40] the temperature in the middle zone. Around the open top of this vessel is an annular trough [3] half-filled with bismuth-lead eutectic alloy. A thermocouple [41] indicates the temperature of the alloy.

The furnace top [5] has a rim [4] extending down into the bismuth-lead seal, so that the top may rise or fall depending on the internal pressure. Should excess pressure suddenly develop, gas may also escape through this molten seal.

A pipe [13] connects the interior of the furnace to an evacuator through a valve [16] and also to a needle valve [17] which controls the supply of hydrogen from a tank [21] through the regulator [20], flow indicator [19], and a reservoir [18]. The pipe [13] which is attached to the top has a heater [27] throughout its length and is enclosed in a protection tube [28]. The internal temperature of this tube is kept above 331°C. to prevent condensation of zirconium chloride. A thermocouple [29] indicates this temperature. A heater [11] provided with insulation [12] is used to keep the top above 331°C.

Fastened to the top is a double set of cooling coils [6], through which may be passed air through a valve [8], or water through a valve [10], and a sight-glass [9] for observing the flow of cooling water. A yoke and hook [25] connect the top by means of a flexible steel cable over pulleys [24] to a counterweight [22] which assists in counter-balancing the zirconium chloride which sublimes in the coils. The position of the top is conveniently indicated to the operator by a pointer [26] fastened to the flexible cable.

About 200 pounds of impure zirconium chloride, as received from the chlorinator, is placed in a thin nickel container [1] 26 inches in height and lowered into the stainless-steel vessel [2]. The top [5] is then lowered into the molten bismuth-lead seal and the seal allowed to solidify. The stainless-steel vessel is then evacuated with a water aspirator to about 25 milli-

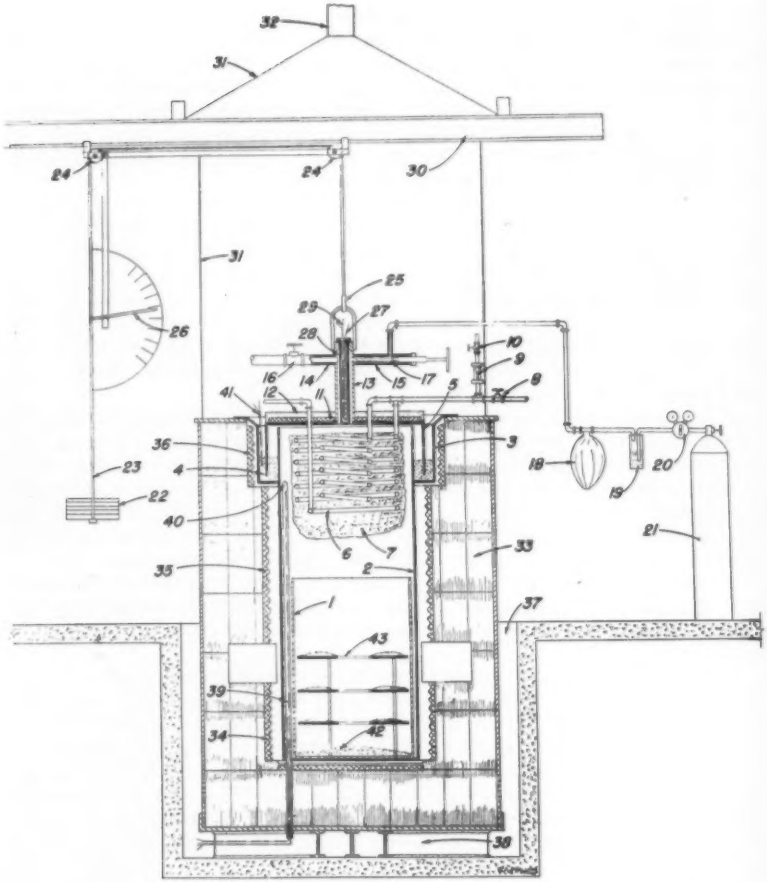

FIG. 2. Apparatus for production of pure dense zirconium chloride

1. Sheet metal container 2. Stainless steel vessel 3. Annular trough 4. Rim of furnace top 5. Furnace top 6. Coils 7. Zirconium chloride 8. Air valve 9. Sight glass 10. Water valve 11. Heater 12. Insulation 13. Pipe connector 14. Pipe (vacuum line) 15. Pipe (gas inlet line) 16. Valve (vacuum line) 17. Needle valve 18. Gas reservoir 19. Flow indicator 20. Regulator 21. Hydrogen tank 22. Counterweight 23. Flexible cable 24. Pulleys 25. Yoke and hook 26. Pointer 27. Heater element 28. Heater well 29. Thermocouple 30. I-beam 31. Sheet-metal hood 32. Exhaust duct 33. Furnace 34. Lower-zone heating unit 35. Middle-zone heating unit 36. Upper heating unit 37. Furnace pit 38. I-beams 39. Lower-zone thermocouple 40. Middle-zone thermocouple 41. Molten seal thermocouple 42. Residue 43. Trays

meters mercury pressure, filled with hydrogen, and then evacuated again. The lower-zone heater [34] is set at 150°–200°C. during this operation to

facilitate removal of residual silicon tetrachloride and also hydrogen chloride, formed by the reaction of atmospheric water vapor with the crude zirconium chloride and the reduction of ferric chloride.

After a second filling with hydrogen, the lower-zone temperature is raised to 400°C. and the bismuth-lead seal melted by means of the upper heating unit [36]. The internal pressure, due to expansion of hydrogen and further evolution of hydrogen chloride from the raw zirconium chloride, is relieved at intervals through a valve [16] during this heating period. Pure zirconium chloride begins to distill at 331°C. and is collected on the air-cooled coils [6] attached to the top. The temperature of the lower zone [34] is gradually raised as the pressure permits. When the sublimed body of zirconium chloride increases in thickness, water is substituted for air as the coolant. Zirconium chloride is deposited as finely divided crystals when condensed on a cold surface, so an attempt is made to keep the condensing surface above 100°C. to obtain the dense form.

After the temperature as indicated by the lower thermocouple [39] has reached 650°C., the internal pressure gradually becomes static and finally decreases because of condensation of practically all the zirconium chloride vapor on the coils. The furnace is then allowed to cool. A light, fluffy residue [42], composed mainly of zirconium oxide and ferrous chloride together with any other nonvolatile impurities, remains in the container. The very light zirconium oxide remaining acts as an excellent heat insulator during the sublimation. To minimize the depth of this insulating layer and increase the rate of sublimation, the charge is supported in the container on three superimposed trays of black iron [43] spaced about 8 inches apart and with central holes about 5 inches in diameter. The raw zirconium chloride is charged through the central holes. During cooling, nitrogen gas is admitted. After the furnace has cooled, the bismuth-lead seal is remelted and the top, with the refined zirconium chloride body on the coils, is removed and weighed. The zirconium chloride is firmly attached to the coils, as shown in Fig. 3, in the form of a cylinder about 14 inches in diameter and 18 inches in length. The results of a typical purification test are shown in Table II.

REDUCTION OF REFINED ZIRCONIUM CHLORIDE WITH MAGNESIUM METAL

After the purified zirconium chloride is removed, the nickel container which originally held the raw zirconium chloride is removed and the stainless-steel vessel is thoroughly cleaned to remove all oxide dust. The reduction step of the operation is carried out in the same furnace and stainless-steel container as the purification step. In this step the pure zirconium chloride on the coils is sublimed to react with molten magnesium forming zirconium metal and magnesium chloride.

A drawing, illustrating the arrangement used, is shown in Fig. 4. The magnesium ingots used for reduction are very carefully cleaned to remove any surface dirt and oxide coating which might contaminate the zirconium metal. A 10 per cent excess of magnesium, over the stoichiometric amount required to react with the zirconium chloride, is placed in an iron crucible [2] 16½ inches high. A weighed charge of magnesium is shown in Fig. 5. The crucible with the magnesium is lowered into the furnace. A radiation shield [6] and a sheet-metal can [7] are then placed in position on top of the

reaction crucible. The top with the attached sublimed zirconium chloride is then replaced, and the bismuth-lead seal allowed to cool. A photograph showing the relationship of crucible, radiation shield, sheet-metal can, and dense zirconium chloride is shown in Fig. 6.

The stainless-steel vessel is evacuated by means of the water ejector pumps and filled with high-purity helium. This operation is repeated in order to insure the removal of all air from the reaction vessel.

FIG. 3. Removing purified zirconium chloride from furnace

The lead-bismuth seal is melted and the lower zone temperature set at 800°C. When the magnesium melts, the middle-zone temperature is slowly raised, and the zirconium chloride gradually sublimed from the coil by careful control of this middle-zone heating unit. The coils are cooled by air or, if evaporation becomes too rapid, by air and water. The temperature of the middle zone is gradually increased until a temperature of 650°C is reached, and no further cooling of the coils is required. The top is kept

TABLE II. *Efficiency of purification of crude zirconium chloride*

Charge			Recovery			
Raw $ZrCl_4$	Purified $ZrCl_4$		Residue (oxide)		Loss (escape as vapor, handling, etc.)	
Pounds	*Pounds*	*Per cent*	*Pounds*	*Per cent*	*Pounds*	*Per cent*
210	206	98.2	3.5	1.7	0.5	0.3

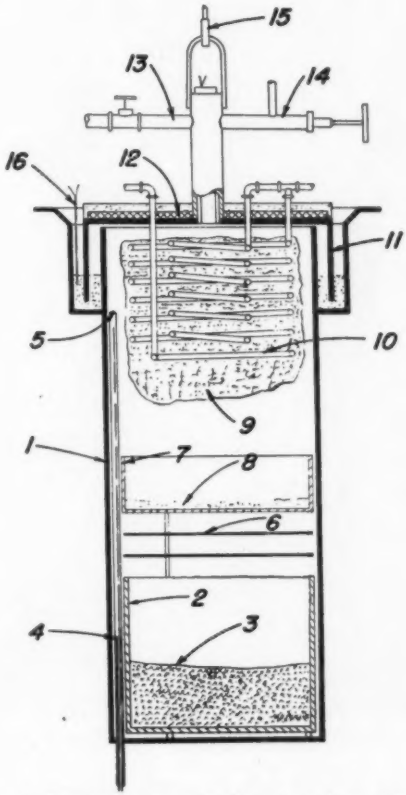

FIG. 4. Equipment for reducing zirconium chloride

1. Stainless steel vessel 2. Iron crucible 3. Magnesium, magnesium chloride, and zirconium 4. Lower-zone thermocouple 5. Middle-zone thermocouple 6. Radiation shield 7. Sheet-metal can 8. Oxide 9. Zirconium chloride 10. Coils 11. Rim of furnace top 12. Heater 13. Pipe (vacuum line) 14. Pipe (gas inlet line) 15. Yoke and hook 16. Bismuth-lead thermocouple (molten seal thermocouple)

above 331°C. by means of the heater [12]. When the reaction is complete, the equipment is allowed to cool. An atmosphere of helium is maintained during cooling. When cold, the reaction crucible containing zirconium metal and magnesium chloride is removed. All loose black dust in or on the crucible is removed by brushing. During the reduction operation, there is apparently a vapor-phase reaction which deposits magnesium chloride mixed with a black dust on the radiation shields and also in the sheet-metal

FIG. 5. Weighed charge of magnesium in iron crucible

can which rests under the coil containing the zirconium chloride. The can is placed in this position to receive any zirconium oxide that might be present on the coil. Zirconium oxide is, possibly, present because a very slight reaction must take place between the moisture of the atmosphere and the surface of the dense zirconium chloride body on the coils during the period while the furnace is open and the dense chloride is exposed.

The sublimation of the zirconium chloride into the magnesium amounts

FIG. 6. Relationship of reaction crucible, radiation shield, sheet-metal can and dense zirconium chloride in reduction step.

TABLE III. *Efficiency of reduction of zirconium chloride with magnesium*

Purified $ZrCl_4$	Mg	Zr in $ZrCl_4$	Zr Obtained	
Pounds	Pounds	Pounds	Pounds	Per cent recovery
2.6	47.5	80.5	75.0	93.2

to an additional purification step as far as any oxide contained in the material is concerned. The results obtained in a reduction test are shown in Table III.

REMOVAL OF MAGNESIUM CHLORIDE AND EXCESS MAGNESIUM BY MELTING AND VACUUM DISTILLATION

A drawing illustrating the equipment used for the removal of the excess magnesium and the magnesium chloride formed in the reduction step is

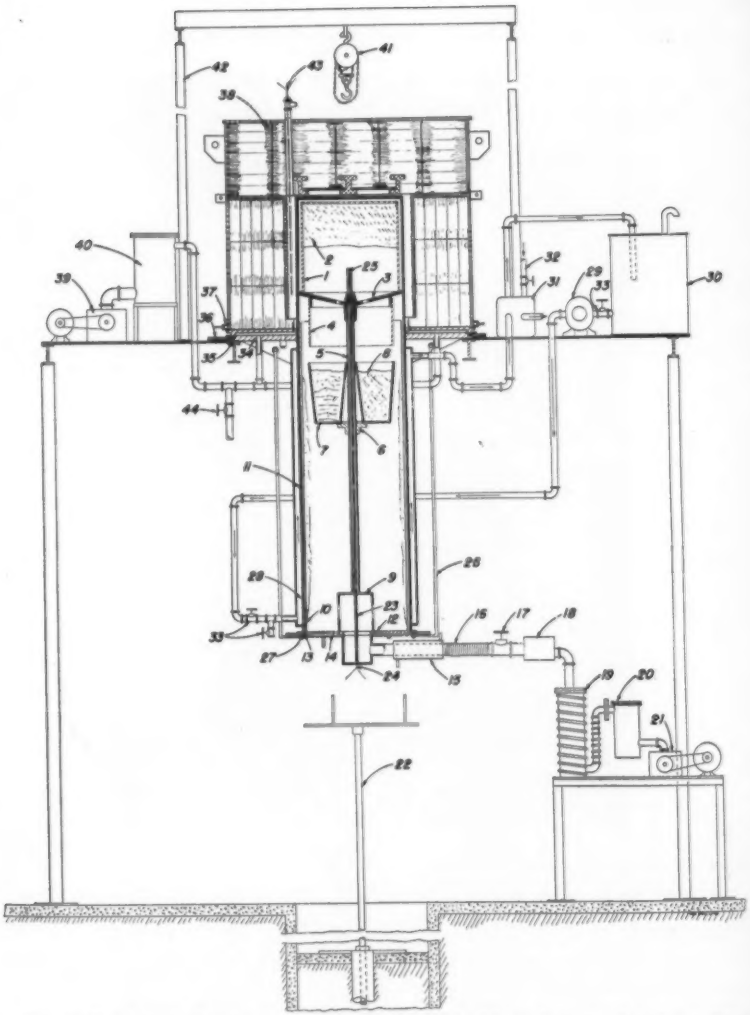

FIG. 7. Equipment for removal of magnesium chloride and magnesium by melting and vacuum distillation.

1. Inverted iron crucible 2. Magnesium chloride, zirconium, and magnesium 3. Perforated collector 4. Sheet metal shield 5. 2-inch stainless steel pipe 6. Collar 7. Stainless-steel can 8. Magnesium chloride 9. Supporting base 10. Stainless-steel shields 11. Retort 12. Bottom plate 13. Vacuum joint 14. Water-cooling 15. Water-cooled pipe 16. Flexible tubing 17. Vacuum valve 18. Dust trap 19. Oil diffusion pump 20. Drying tower 21. Mechanical vacuum pump 22. Hydraulic ram 23. Thermocouple tube 24. Thermocouple leads 25. Thermocouple 26. Clamps 27. Water-cooling 28. Oil-cooled jacket 29. Oil circulating pump 30. Oil reservoir 31. Heat exchanger 32. Water-cooling 33. Oil valve 34. Vacuum connection 35. Vacuum joint 36. Water-cooling 37. Water-cooling 38. Furnace 39. Mechanical vacuum pump 40. Drying tower 41. Chain block 42. I-beam frame 43. Furnace thermocouple

shown in Fig. 7. The retort [11] is 20 inches in diameter and 78 inches in length. Its closed end extends 24 inches into the furnace [38]. The lower portion of the retort has a jacket [28] which is cooled by circulating through it a light oil by means of pump [29] from a reservoir [30] through a valve [33]. Oil is used as it is considered less dangerous than water should a leak develop into the evacuated vessel. To cool the oil, a water-cooled [32] heat exchanger [31] is provided.

Two vacuum systems are used. One outer system, consisting of a mechanical vacuum pump [39] and drying tower [40], is connected to the heating portion of the furnace [34]. This pump reduces the external pressure on the outside of that portion of the retort which is in the hot zone of the furnace to about 1 mm. of mercury and prevents the retort from collapsing at elevated temperature. A vacuum-tight joint [35] seals the furnace shell and is protected by water-cooling [36], [37].

The internal vacuum system includes a mechanical vacuum pump [21], a drying tower containing phosphorus pentoxide [20], an oil diffusion pump [19], a dust trap [18], vacuum valve [17], flexible tubing [16], and a water-cooled pipe [15] which communicates with the inside of the retort through several holes in the support [9].

The bottom plate [12] makes a vacuum-tight seal [13] with the retort. The entire bottom plate, as well as the rim, is water-cooled, [14], [27]. A protection tube [23] encloses a thermocouple [24] which extends to the top of the support tube [25]. A supporting base [9] has fastened to it a 2 inch stainless-steel tube [5] to which is pinned a collar [6] supporting a stainless-steel can [7] used to receive the molten magnesium chloride. On top of the tube [5] is placed a perforated grid [3] which supports the inverted iron crucible [1] containing zirconium, magnesium chloride, and excess magnesium. Stainless-steel condensing shields [10] are placed inside of the retort to collect the magnesium chloride and magnesium, which otherwise would condense on the walls.

In assembling the internal unit, the bottom plate [12] is attached to the hydraulic ram [22] and the inverted iron crucible is placed on top of the perforated grid [3]. As the unit is lifted into the furnace by means of the hydraulic ram, the stainless-steel shields are placed in position. After the unit has been raised into the operating position, it is held in place by six clamps [26] which swing in and under the bottom plate. The asembled unit about to be raised into the retort is shown in Fig. 8. After the internal pressure is reduced by the vacuum pumps to a few hundredths of a micron, power is applied to the furnace. The recording and controlling potentiometer is set for 800°C. At about 750°C., the magnesium chloride melts and runs down through holes in the perforated grid [3] into the stainless-steel can [7].

When the temperature, as measured by the internal thermocouple [25], reaches about 775°C., there is usually an evolution of hydrogen which may last for an hour or more. This hydrogen may have been introduced by the magnesium metal. After the evolution has taken place the temperature is raised slowly until the inner thermocouple [25] registers 885°C. It is held at this temperature for several hours to remove the last traces of magnesium and magnesium chloride.

After the furnace is cooled to about 300°C., high-purity helium is ad-

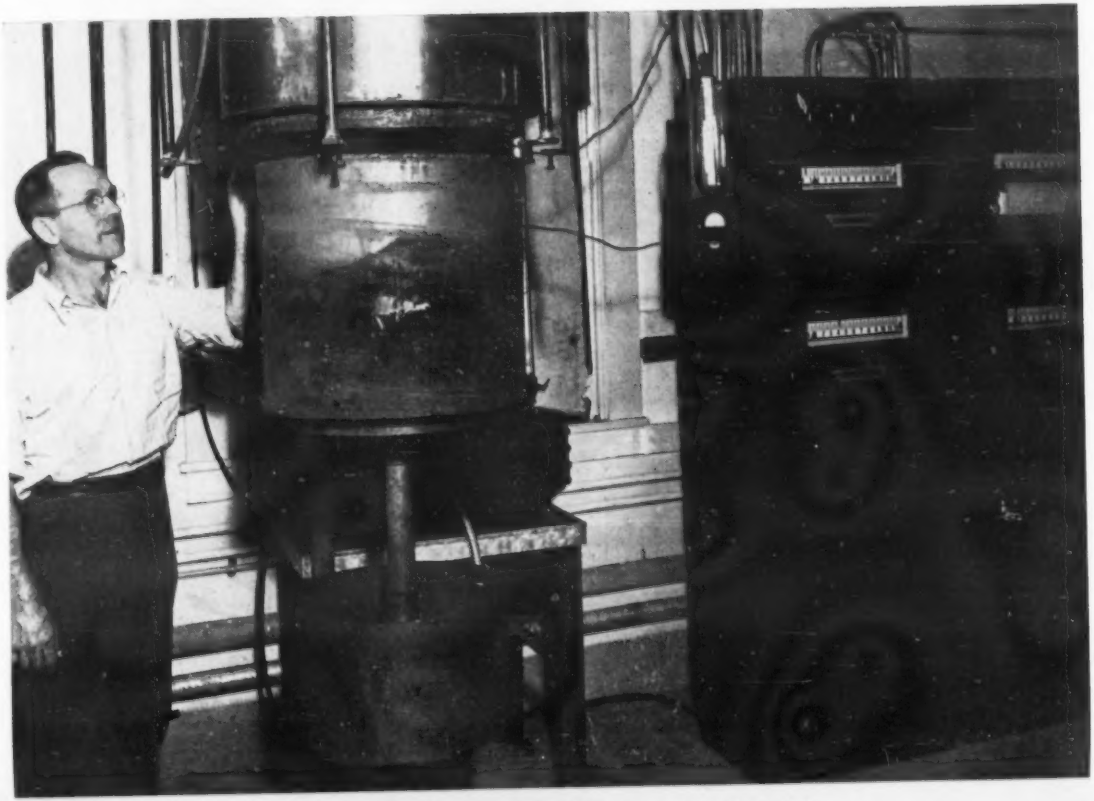

FIG. 8. Assembled unit about to be raised into the retort

mitted to the inner portion of the asembly and air to the outer chamber. When the contents of the furnace have reached room temperature, dry air is introduced into the retort by withdrawing a small amount of helium and replacing it with air. This is repeated a number of times until air replaces the helium. The zirconium sponge is gradually conditioned with air in this manner to minimize the zirconium fire hazard when the metal is removed from the furnace. Some danger still exists because of the finely divided magnesium that is attached to the shields.

The unit is removed from the retort by means of the hydraulic ram [22]. The bulk of the magnesium chloride is found in the can [7] directly under the perforated grid [3].

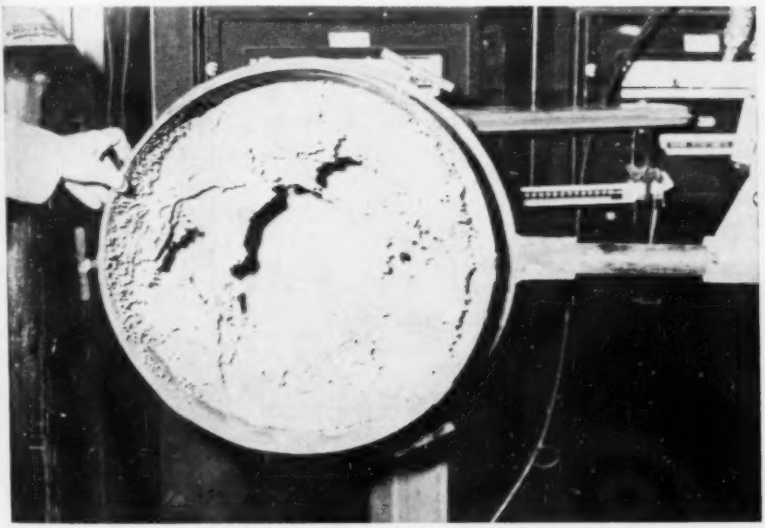

FIG. 8. Assembled unit about to be raised into the retort

FIG. 9. Zirconium metal in iron crucible

High-purity zirconium remaining in the iron crucible, Fig. 9, is in two different forms—(a) a spongy mass near the middle of the crucible and (b) as a more dense but still porous metallic deposit in a ring around the bottom. The metal is removed and broken into pieces of desired size.

FUSION OF THE ZIRCONIUM

The first successful method of melting zirconium was by use of a vacuum-arc furnace which has been described previously (2). It was subsequently demonstrated that zirconium could be melted in the presence of massive graphite without reacting appreciably with it. A test furnace therefore was constructed, using a split-graphite resistor heating element (3). This furnace produced ingots having good ductility and low hardness.

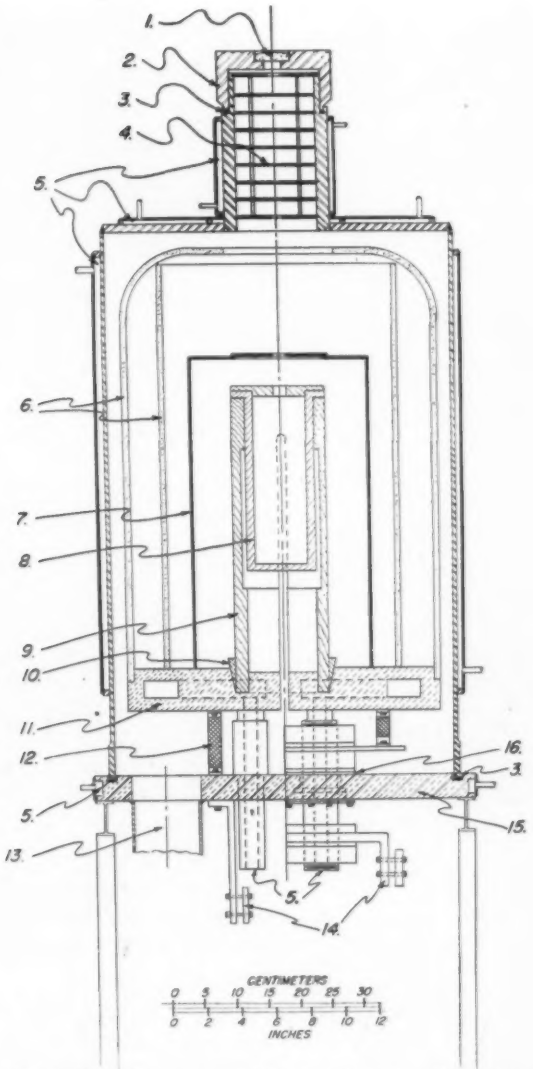

FIG. 10. Details of vacuum resistor furnace for melting zirconium

1. Quartz observation window 2. Closure cap 3. Rubber gasket 4. Steel baffles 5. Water-cooling 6. Fused silica shields 7. Molybdenum shields 8. Graphite crucible 9. Graphite resistor 10. Copper wedges 11. Water-cooled resistor clamp 12. Flexible power cables 13. Vacuum connections 14. Power input connections 15. Brass bottom plate 16. Micarta insulation

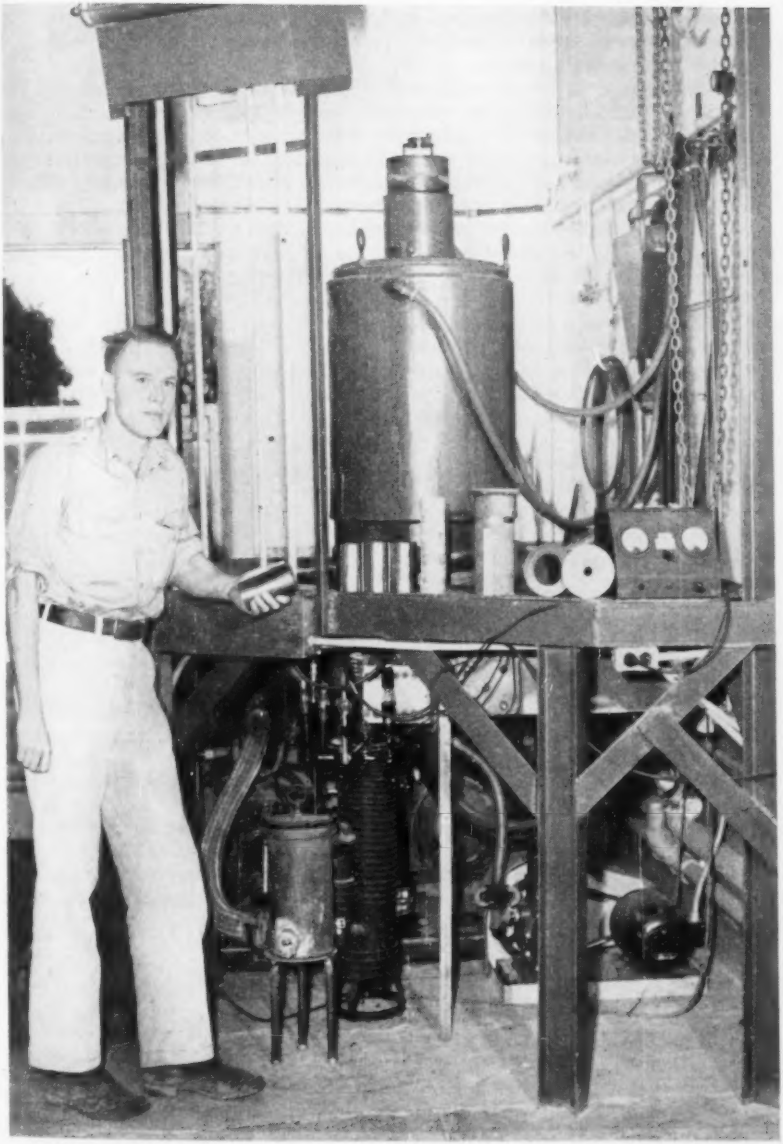

FIG. 11. General arrangement of melting furnace and vacuum systems with products

On the basis of the results obtained with the small resistor furnace, a larger furnace of the same general type was designed and built. The details of the furnace are shown in Fig. 10.

The split-graphite tube resistor [9] is placed in the water-cooled resistor clamps [11] and held in place by copper wedges [10]. Power is supplied to these clamps through flexible cables [12] and a water-cooled copper bar insulated by carefully ground micarta seals [16]. A vacuum connection [13] is provided at the bottom of the furnace. A graphite crucible [8] with its cover is placed inside the graphite resistor [9]. A molybdenum shield [7] and two fused silica shields reduce the heat losses to the water-cooled furnace jacket [5]. Steel baffles [4] containing sighting holes are suspended in the neck of the furnace and assist in eliminating heat radiation to the observation window [1]. The outer shell of the furnace is made vacuum-tight by means of a rubber gasket [3] placed in a recess in the bottom brass plate [15]. A closure cap [2] containing a quartz observation window [1] enables the operator to place and remove crucibles in the resistor without removing the entire jacket. The quartz observation window enables the operator to determine temperatures and progress of melting.

TABLE IV. *Characteristics of ingots from large resistor furnace*

Ingot No.	Wt., Pounds	Hardness, Rockwell B	Carbon, Per cent
1	6	72	0.16
2	7.5	76	.14
3	5	68	.15
4	10	74	.19
Average			.16

The furnace is evacuated by a 6-inch-diameter oil diffusion pump in series with a duplex, single-stage mechanical pump having a theoretical displacement of 110 cubic feet per minute.

The power applied to the furnace at the bus-bar fittings [14] is obtained from two 40-KVA transformers connected in series. In order that a maximum weight per charge may be placed in the melting crucible, the sponge is compressed in a cylindrical die at about 20 tons per square inch.

Melting crucibles of dense graphite are degassed for about 20 minutes in the furnace at 1,850°C. to 0.01 micron. After cooling, the degassed crucible is loaded with briquets and again placed in position in the resistor. Fusion of the zirconium is carried out with a power input of about 53 kw. (17 volts, 3100 amperes a.c.) in the range of 0.01 micron. Fusion is complete in about 20 minutes for an 8-pound melt. The melt is allowed to freeze and cool in the crucible. The crucible is removed from the ingot by turning the graphite off in a lathe.

Fig. 11 shows the general arrangement of the furnace and evacuating system. The back of the control panel is shown in the upper left of the photograph. Also shown are four finished zirconium ingots, a stack of zirconium sponge briquets as charged to the furnace, and two views of the graphite crucibles and lids used in melting.

The characteristics of the first four ingots melted in this furnace are shown in Table IV.

Impurities in the melted metal in addition to carbon are generally, iron 0.025 per cent, nitrogen 0.04 per cent, magnesium less than 0.01 per cent, and chlorine less than 0.005 per cent.

In the forging of zirconium ingots, the cast structure is usually broken up by hot working. Zirconium may also be rolled, swaged, and drawn without the use of a protecting sheath, if the annealing temperature is not taken to the point where the zirconium oxide formed diffuses and dissolves in the

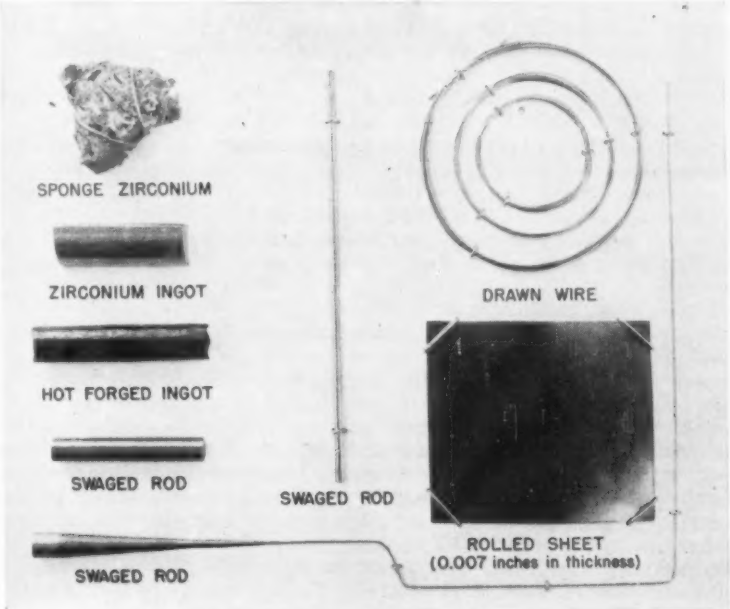

FIG. 12. Photograph showing various zirconium articles

zirconium metal causing it to become brittle. Experience has indicated that about 600°C. is the maximum temperature which may be used. If the working operation is to be carried out above 650°C., it is desirable to encase the zirconium ingot in an iron jacket. Large ingots have been forged with an air hammer and subsequently rolled to plate. The temperature of working the iron sheathed zirconium must not exceed approximately 925°C., as iron and zirconium alloy at about this temperature. The eutectic composition contains about 17 per cent iron.

To remove the oxide coating from the metal, it is first necessary to break the coating by rolling or swaging. Very dilute hydrofluoric acid may then be used to remove the adherent oxide scale. The zirconium oxide film is

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very hard and insoluble in hydrofluoric acid. Its removal appears to be due to dissolution of an extremely small amount of zirconium at the interface. Subsequent treatment such as wire brushing may also be used. Sheet 0.005 inch thick and wire approximately the same in diameter have been prepared by this method. A photograph of various zirconium articles is shown in Fig. 12.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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COATING STEEL WITH NICKEL BY IMMERSION IN NICKEL CHLORIDE SOLUTIONS[1]

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ABSTRACT

A simple method for depositing controlled amounts of nickel on steel by chemical displacement from a hot nickel chloride, boric acid solution is described. Deposits up to 30 millionths inch (0.75 micron) in thickness can be readily produced in this way. Suitable heat treatment of these deposits renders them compact and adherent and at the same time causes diffusion of the nickel and iron. Although steel coated in this way rusts readily, its surface is altered sufficiently to suggest that it will serve as a better basis for other coatings such as organic finishes, conversion coatings, ceramic enamels and perhaps for other metallic coatings. The optimum degree of alloying of the nickel and iron varies with the intended use of the product.

INTRODUCTION

A great amount of attention has been focused in recent years on the protective value of nickel coatings on steel. The evidence is clear that the only practical way to insure high protective value and freedom from porosity is to specify adequate thickness of the coating. To illustrate modern requirements, the 1946 specifications for plated coatings on automobile bumper bars in one large motors company call for a minimum total thickness of 0.00225 inch (2250 millionths inch) (56 microns) of copper, nickel, and chromium. Progress along this line seemed fairly satisfactory and the thought occurred that, in concentrating all efforts on reducing porosity, perhaps some potential uses for very thin coatings were being neglected.

[1] Manuscript received April 1, 1948. This paper prepared for delivery before the New York Meeting, October 13 to 16, 1948.

It was felt that if an inexpensive process for preparing nickel coatings only 10 to 100 millionths inch (0.25 to 2.5 microns) thick were developed then steel with its surface ennobled in this manner might serve as a better basis metal for other coatings such as organic finishes, conversion coatings, ceramic enamels, or even tin.

It was decided to study the chemical displacement of nickel by steel because of the simplicity of such a process and the inexpensive equipment needed to carry it out.

PREVIOUS WORK

Metal deposition by chemical displacement has been used from relatively ancient times for the production of thin coatings of gold and, in later years, of numerous other metals. The only large scale process in which nickel is displaced from solution by steel is the nickel dip or nickel flashing treatment employed in the ceramic enameling industry. This is commonly carried out by simple immersion of the pickled steel in a dilute solution of nickel sulfate or nickel ammonium sulfate and boric acid for not more than 10 minutes at temperatures near 160°F. (70°C.). The bath usually contains $\frac{3}{4}$ to 2 oz. nickel sulfate per gallon (5.6 to 15 g.p.l.). Some operators add $\frac{1}{4}$ oz. boric acid (2 g.p.l.). The pH of the solution was formerly kept high, in the neighborhood of pH 6, but the recent trend is toward a lower value between 3 and 4 in order to displace a greater weight of nickel without increasing the treatment time (1).

A variety of factors must be controlled in order to insure that the desired amount of deposit is obtained. These are pretreatment of the steel, time, temperature, pH, concentration, amount of iron salts present in the bath, and the amount of agitation provided. In spite of such control, the deposition is often erratic from plate to plate (2). After removal of the steel from the nickel dip it is customarily rinsed in cold running water and then immersed in a "neutralizer" solution containing sodium carbonate and borate or else containing $\frac{1}{4}$ per cent sodium cyanide. The object of this treatment is to prevent rusting during drying of the steel and prior to application of the first ceramic coat.

The weight of nickel required to develop maximum adhesion of enamels on steel varies with the steel composition and the type of enamel but is near 0.05 to 0.09 grams per sq. ft. (5.4 to 9.7 milligrams per sq. dm.). This weight represents an average thickness of nickel of only 2 to 5 millionths inch (0.05 to 0.09 microns).

Until a short time ago, there was no certainty as to the nature of the nickel deposit. Some held the opinion that it was a nickel oxide, some a basic compound, and others that it was metallic nickel. The work of Wainer and Baldwin (2) established that these extremely thin deposits are essentially metallic in nature.

A recent patent (3) indicates that a thin layer of immersion nickel deposited from an acidified nickel chloride solution is helpful in securing good adhesion of silver to steel in making aircraft engine bearings.

From the information available on the subject it seemed worthwhile to attempt to form heavier nickel deposits by simple immersion through the use of more concentrated solutions and perhaps through use of other anions than the sulfate.

PRELIMINARY EXPERIMENTAL WORK

A survey of the behavior of steel in solutions of nickel ammonium sulfate, nickel nitrate, acetate, sulfate, and chloride led to the conclusion that the chloride was the most promising of these reagents. It gave better looking, more compact deposits than did solutions of the other salts. Under some conditions weights of nickel corresponding to thicknesses as great as 90 millionths inch (2.3 microns) were obtained and there was no question but that these deposits were metallic. The coated steel rusted so readily that it could not be stored in ordinary indoor atmospheres. It was discovered, however, that annealing in a reducing atmosphere overcame this difficulty.

The conditions maintained during the period of immersion of the steel influence the reaction as follows:

1. Deposition proceeds more rapidly with rise in temperature.
2. The rate of deposition increases with increase in concentration of nickel chloride.
3. Increase in pH of the solution increases the rate of deposition of nickel but blistering and peeling of the annealed deposits is encountered if this change is carried too far. A concentrated solution can be operated at a higher pH than a dilute bath.
4. To aid in controlling the pH a buffer is desirable. Acetic acid is satisfactory but boric acid is preferable since it is less volatile.
5. Motion of the steel is desirable because it leads to more uniform deposition over the specimen surface.
6. The nature of the basis metal has some effect upon the porosity of the deposit. Good results are obtainable with tin mill black plate or other cold rolled steel.
7. Accumulation of much ferrous chloride or ferric hydrate in the solution leads to excessive porosity of the annealed deposit.
8. The efficiency of the process is close to 100 per cent if calculated on the basis that it is a simple displacement reaction:

$$Fe + Ni^{++} = Ni + Fe^{++}$$

PREPARATION OF NICKEL-COATED STEEL

A large number of specimens were prepared for study of the properties of the coated steel. The procedure by which they were made was developed in the preliminary study just described. The laboratory process recommended by the authors for coating steel with nickel by immersion is as follows:

Steel base

Since the nickel coatings are thin they reflect the condition of the steel surface. They are as bright as the metal upon which they are plated. Any smooth clean surface seems suitable, but it should be free of inclusions or non-conducting areas. It is known that the steel base affects the thickness and porosity of the nickel coatings. Except in the outdoor exposure tests, the basis metal used in all the experimental work was commercial tin mill black plate, 0.011 inch (0.028 cm.) thick. The specimen size varied from 3 by 5 in. (7.6 by 12.7 cm.) to 8 by 11 in. (20 by 28 cm.).

Cleaning the steel

Good results have been obtained by pumice scrubbing, rinsing, placing

the steel in a nickel wire rack, and then treating as cathode for 2 min. at 10 amp./sq. ft. in a hot solution containing 60 g./l. of sodium carbonate and 15 g./l. of sodium hydroxide. The current is applied through the rack. After the cathodic treatment the steel is rinsed thoroughly and then immersed while still wet in the nickel chloride bath.

Other cleaning procedures would probably be satisfactory, but care must be taken to avoid setting up large anodic areas on the steel surface immediately before coating. A sulfuric acid pickle, shortly before immersing in the nickel bath, resulted in an uneven sporadic nickel coating, presumably because the pickling formed large anodic areas. If an acid pickle is used, it seems desirable to follow it with a pumice scrub and a dip in an alkaline cleaner. If the specimens are fairly clean, the use of current in the alkaline cleaner is not necessary.

Bath composition

Nickel chloride	600 g.p.l. (80 oz./gal.)
Boric acid	30 g.p.l. (4 oz./gal.)
pH	3.5 to 4.5
Temperature	70°C. (160°F.)
Motion	Desirable but not essential

Commercial salts of a grade suitable for nickel plating baths can be used. The high concentration of nickel provides for easy control of the bath. It can be allowed to drop to 300 g.p.l. without harm but if it becomes much lower the rate of nickel deposition decreases and becomes more dependent upon pH.

Under the preferred conditions, the pH range could be considerably extended, but the specified 3.5 to 4.5 permits greater latitude in nickel chloride content. As the pH is lowered below 2.5, the rate of nickel deposition decreases.

Motion is desirable but not necessary. Moving the steel in a vertical circular path at a rate of 16 ft./min. (4.9 meters per min.) causes uniformity in the nickel coat. Lack of motion can be compensated to some extent by increasing the volume of the bath. Aeration should be avoided since this oxidizes the ferrous salts formed in the displacement reaction.

The rate of nickel deposition increases with temperature increase so a hot solution is specified. Above 160°F. (70°C.) the problem of finding a suitable tank material becomes too difficult. Lead corrodes rapidly in this solution. Rubber-lined steel, hard rubber, Pyrex glass, and cast high silicon irons can be used successfully.

Thickness of nickel coating

The thickness of the nickel coating increases with the time of immersion. It also depends on other uncontrolled variables such as the surface of the steel. Experience gained by coating over 850 pieces of 13 heats of steel indicates the order of thickness as shown in Table I.

If the average points are plotted, the curve in Fig. 1 is obtained. The initial rate of deposition is equivalent to about 5 amp./sq. ft. (0.5 amp./sq. dm.). After 2 minutes the rate begins to decrease, but apparently it never becomes zero although it becomes prohibitively slow. After an immersion

time of 23 hours, the thickness of the nickel coat was about 90 millionths inch (2.25 microns).

The best method of determining the thickness of the nickel coat is to strip the nickel by immersing the specimen in cold concentrated nitric acid overnight and analyzing the solution for nickel. This avoids contaminating the analytical sample with nickel from the steel base. For the most accurate results the nickel should be stripped before any heat treatment.

TABLE I. *Thickness of nickel coating*

Immersion Time	No. of Pieces Analyzed	Millionths inch of nickel			Microns, Ave.
		Max.	Min.	Ave.	
30 sec.	14	2.8	1.1	1.7	.042
100 sec.	12	8.6	4.5	6.7	.168
2 min.	14	9.3	3.3	7.1	.178
5 min.	61	30	8	14.4	.360
45 min.	17	47	15	26.0	.650

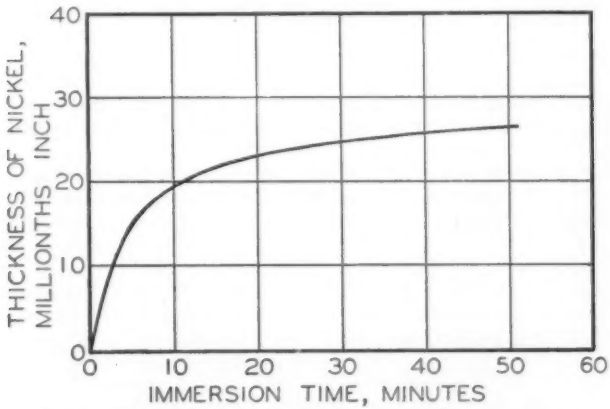

FIG. 1. Thickness of nickel coating as a function of time

As compared with electroplating, immersion coating affects all parts of the specimen identically. There is no problem of throwing power and the deposit is not thicker at the edges.

Maintenance of the bath

For deposition of nickel to occur, iron, equivalent to the amount of nickel displaced, must dissolve in the solution as ferrous iron. This then becomes oxidized to ferric iron and precipitated as ferric hydroxide. In order to maintain a constant pH, the hydrochloric acid thus liberated must be neutralized. To maintain a minimum porosity in the nickel coating, the pre-

cipitate must be removed. Of course the nickel must be replaced and attention paid any drag out.

On a laboratory or small scale, the bath can be adjusted periodically by adding nickel hydroxide or nickel carbonate to replenish the nickel and raise the pH, by aerating overnight to precipitate the iron, and by filtering.

On a commercial scale, it would be desirable to remove the iron continuously. This could be done by withdrawing a portion of the solution and treating as above. Or, the portion could be aerated and filtered to remove the iron, then the nickel replenished and the pH raised by passing the filtered solution through a column fitted with finely divided nickel. Vigorous agitation with steam shattered nickel shot would accomplish the same purpose.

Drying after immersion in the nickel bath

The immersion deposits are quite porous. To prevent rusting and staining, they must be rinsed and dried quickly. A water or dilute acid rinse is necessary to remove nickel and iron chlorides, and then a rinse in hot 2 per cent ammonium hydroxide solution is helpful. On a small scale, the material can then be dried with clean cloths. On a large scale, a hot air blast should be satisfactory. Hot, thick steel contains enough heat to facilitate drying.

HEAT TREATMENT

A high temperature treatment in a reducing atmosphere serves to sinter the nickel coating, to decrease porosity, and to increase adhesion. It is possible to detect improvement in these respects after heating at 600°C. (1100°F.) for as short a time as 30 minutes. The extent to which these changes occur appears to be influenced by both temperature and time. Peculiarly enough, a relatively mild treatment is desirable for some types of use, as will be shown later, whereas for others a long time at a temperature as high as 760°C. (1400°F.) is preferable. The temperature and time cycle will be indicated for each experiment described.

Coatings over 20 to 30 millionths inch (0.5 to 0.75 microns) thick blister if heated rapidly; this tendency to blister increases with rise in pH of the immersion bath. The annealing treatment gives the surface of the nickel coating a white matte appearance. A metallographic cross-section through a typical nickel immersion coating after a mild 30 minute anneal at 650°C. (1200°F.) is shown in Fig. 2.

As an example of a long time treatment, the following cycle can be used which simulates a commercial steel-mill box-anneal: heat slowly in a non-oxidizing, sulfur-free atmosphere to 650°C. (1200°F.) for about 27 hours, hold at 660°C. (1220°F.) for 15 hours, and cool to 177°C. (350°F.) for 48 hours.

PROPERTIES OF NICKELIZED STEEL

Ductility

Upon severely bending a specimen of coated steel after heat treatment, the surface alloy layer cracks but does not flake off. This effect is illustrated in Fig. 3 for a coating which had been annealed in hydrogen at 650°C.

(1200°F.) for 45 minutes. On the inside of the bends, the coating followed the folds in the steel surface.

Porosity

As indicated previously, immersion deposits rust readily, but develop sufficient corrosion resistance during heat treatment to withstand ordinary indoor storage conditions. Like thin tin coatings, the nickelized surface

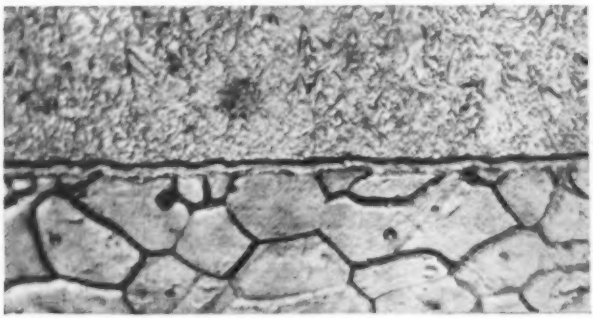

FIG. 2. Cross section through annealed nickel deposit 30 millionths inch thick
Etchant: 2% nital 1500 ×

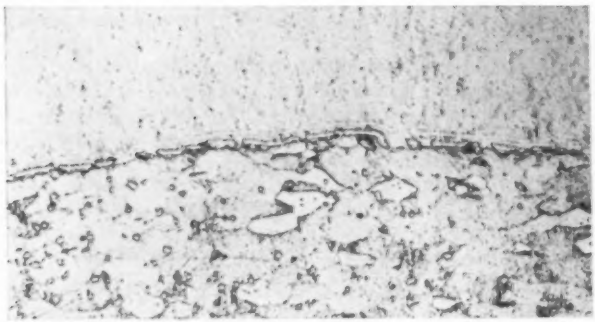

FIG. 3. Cross section through bent annealed nickel deposit 14 millionths inch thick
Etchant: 2% nital 1500 ×

should be oiled with palm or cottonseed oil to avoid rusting in shipment or prolonged storage.

Hot water porosity tests (4) were made by exposing oil-free, nickelized specimens to distilled water acidified with hydrochloric acid to pH 5. A new variable in this test was encountered. When the water was heated to 95°C. and the specimens immersed, they soon became rust-spotted; when the water was overheated and allowed to boil for a short time before reducing the temperature to the desired value of 95°C., the specimens then im-

mersed remained bright for hours. This was presumably due to removal of dissolved oxygen and possibly other gases during the boiling. Care was therefore taken not to overheat the water.

The hot water test of nickelized steel, with coatings of 14 to 30 millionths inch (0.35 to 0.75 microns) which had been annealed at 650°C. (1200°F.) for 45 minutes, developed pores ranging in number from 9000 to 11000 per sq. dm. The pore count on the specimen, shown in Fig. 4, was about 6000 per sq. dm. The nature of the steel base appeared to have a greater effect upon porosity than did the weight of nickel deposited. One batch of steel gave very poor results with pore counts running from 10,000 to 100,000 per sq. dm., but no explanation for its behavior was found and no similar heat of steel was encountered.

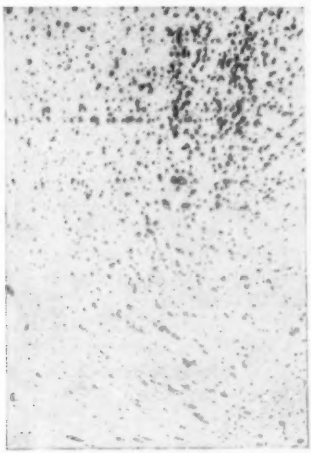

FIG. 4. Results of hot water porosity test on steel coated with an annealed nickel immersion deposit, 15 millionths inch thick. Rusting indicated porosity. Actual size

It is evident that the porosity of these nickel deposits is too great to permit their use without further modification in applications where rusting must be avoided. This limitation may play very little part in possible utilization of nickelized steel as a base for other coatings such as ceramic enamels, organic and conversion coatings, and outer layers of tin or zinc. For example, patents issued to The Pyrene Co., Ltd. (5) and to H. T. Davies (6) claim improved coatings for steel in which a thin nickel deposit forms the base for a phosphate coating.

OUTDOOR ATMOSPHERIC TESTS

In outdoor atmospheres the nickelized steel specimens begin to rust as quickly as bare steel and continue to rust. However, the diffused, nickel-iron coating has a marked influence upon the appearance and protective value of the rust coating which develops. The rust coating is darker, thinner, and of finer texture, and the weight loss is greatly reduced.

This was shown by some exposure tests in industrial and marine atmospheres. The industrial location was in the yard of this laboratory at Bayonne, N. J., not far from a center of oil refining activity. The marine location was at Block Island, R. I., about 15 miles from the mainland and remote from manufacturing centers. The specimens were 4 x 6 in. and were mounted on metal racks at an angle of 30 degrees from the horizontal, facing south. The specimens were supported by porcelain insulators which prevented contact with any metal.

The exposure tests were made on 2 heats of steel of the following analyses:

Steel	C,%	Mn,%	Si,%	S,%	P,%	Cu,%	Ni,%	Cr,%
A	0.085	0.43	0.005	0.051	0.103	0.01	0.002	0.02
B	0.043	0.39	0.007	0.020	0.007	0.05	0.01	0.07

Steel A was a low-copper, high phosphorus Bessemer steel, 0.06 in. thick. Steel B was a low-copper, low-phosphorus open hearth steel, 0.03 in. thick.

The specimens were pickled, pumice scrubbed, dipped in an alkaline cleaner, and then given an immersion nickel coat. The thickness of the coating was determined by analysis of control specimens. The specimens were then heat treated in hydrogen for the temperatures and times in Table II. The exposure results are included in Tables II and III.

It is evident that the 48-hour diffusion anneal brought about a decided decrease in the weight losses and pit depths. Further, the thicker nickel coatings were more beneficial than the thinner. The short half-hour heat treatment was only slightly beneficial. All the results were affected by the composition of the steel base and by the location of the exposure. The results have been explained (8) on the basis that the iron-nickel alloy, which is formed during the diffusion heat treatment, corrodes and introduces beneficial corrosion products into the rust coating, making it more protective.

LACQUERED NICKELIZED STEEL

Indications that nickelized steel may have merit as a base for organic coatings were obtained in tests[2] involving exposure in a constant-temperature, constant-humidity room. The temperature was 21°C. (70° F.) and the relative humidity was 65 per cent. As little as seven millionths inch of nickel prevented "underfilm" corrosion of panels of nickelized steel coated with baked, Vinylite-type lacquer during an exposure period of 10½ months, provided that a mild annealing treatment of 45 minutes at 650°C. (1200°F.) had been used in preparing the nickelized steel. In another test of 22 months duration, the results showed that 14 millionths inch (0.35 micron) of nickel substantially retarded corrosion of bare nickelized steel and practically prevented corrosion under Vinylite films. A few panels with Vinylite and phenolic-type films were allowed to remain in the constant conditions room for four years and continued, throughout

[2] The authors gratefully acknowledge the cooperation of the Stoner-Mudge, Inc. Protective Coatings Fellowship at Mellon Institute of Industrial Research, Pittsburgh, who carried out these tests.

TABLE II. *Corrosion of nickelized steel in Bayonne atmosphere*

Specimen area:	3.15 sq. dm.
Date exposed:	May 14, 1942
Steel A:	0.01%Cu, 0.103%P, 0.06 inch thick
Steel B:	0.05%Cu, 0.007%P, 0.03 inch thick

	Steel A				Steel B	
Coating Thickness, millionths inch:	None	20	20	40	None	20
Heat Treatment						
Temp. °F.		1200	1400	1400		1400
Time, hr.		0.75	48***	48***		48***
Loss in weight, mdd						
1.08 years	42.3	28.0	8.9	7.8	13.0	9.2
2.01 "	30.7	20.8	6.5	6.8	8.9	6.2
2.99 "	32.1	32.6	5.8	4.9	7.3	5.1
4.10 "	27.9	30.6	5.1	5.0	6.2	4.8
5.02 "	b	21.2	5.1	4.1	5.9	4.2
Pit Depth, inch*						
1.08 years	0.013	0.014	0.010	0.008	0.008	0.010
2.01 "	0.025	0.028	0.012	0.012	0.011	0.011
2.99 "	a	a	0.015	0.012	0.014****	0.010
4.10 "	a	a	0.020	0.019	a	0.015
5.02 "	b	a	0.021	0.018	a	0.015**

* Average of 8 deepest pits
(a) Perforated
(b) Corroded away
** Three tiny perforations
*** Specimens brought to temperature slowly over a period of 10 hours. Cooling time was also 10 hours
**** One tiny perforation

TABLE III. *Corrosion of nickelized steel in Block Island atmosphere*

Specimen Area:	3.15 sq. dm.
Date Exposed:	July 8, 1942
Steel A:	0.01%Cu, 0.013%P, 0.06 inch thick
Steel B:	0.05%Cu, 0.007%P, 0.03 inch thick

	Steel A				Steel B	
Coating Thickness, millionths inch	None	20	20	40	None	20
Heat Treatment						
Temp. °F.		1200	1400	1400		1400
Time, hrs.		0.75	48***	48***		48***
Loss in Weight, mdd						
1.15 years	58.5	44.1	9.4	6.4	14.4	7.1
2.17 "	58.1	49.9	10.2	5.7	12.5	7.4
2.91 "	b	33.8	13.9	7.0	11.3	6.7
3.90 "	b	b	20.7	8.6	11.6	6.5
4.97 "	b	b	b	23.2		10.7
Pit Depth, inch*						
1.15 years	0.022	0.020	0.017	0.005	0.008	0.007
2.17 "	a	a	0.032	0.019	a	0.015
2.91 "	b	a	a	0.031**	a	a
3.90 "	b	b	a	a	a	a
4.97 "	b	b	b	a	b	a

(a) Perforated
(b) Corroded away
* Average of 8 deepest pits
** One tiny perforation
*** Specimens brought to temperature slowly over a period of 10 hours. Cooling time was also 10 hours.

this period, to prove the advantage of the nickelized steel as a base for the organic coatings.

NATURE OF THE PROCESS

A good discussion of the theoretical aspects of displacement coatings is available in a paper by Roberto Piontelli (7). There appear to be several types of processes involved resulting in different characteristics of the deposit. In the present work there was no evidence of formation of spongy deposits, so that it is probable that a simple mechanism is involved. The structural characteristics of immersion deposits are generally good for metal pairs which are not too far apart in the EMF series. Deposition of nickel probably commences at local cathodic points of the steel surface making them even more cathodic. The anode areas would thus be self-perpetuating. The fact that the rate of deposition falls off rapidly with time indicates, however, that anodic polarization occurs or that concentration polarization becomes significant within the pores leading from the anodic areas. It is interesting that the nickel coatings can continue to build up so that a thickness as great as 90 millionths inch (2.3 microns) can be deposited in a bright, metallic form.

The heat treatment, which was found to improve the quality of the coatings so greatly, undoubtedly involves diffusion of nickel and iron. The extent of this alloying is probably small in the mild heat treatment, but in the long "box-annealing" cycle iron diffuses to the outer surface. Specimens of nickelized steel which had been subjected to the box-annealing cycle were submitted to Wainer and Baldwin for use in their study of enamel adhesion (2). Their work showed quite definitely that the surface layer on the steel was a nickel-iron alloy rather than pure nickel, so that considerable diffusion must have occurred.

The fact that the resistance to rusting is greatly improved by heat treatment suggests that there is diffusion not only in a direction normal to the steel-nickel interface, but also in a lateral direction, leading to some alloying of the previously bare anodic spots.

CONCLUSIONS

1. Nickel coatings up to 30 millionths inch (0.75 microns) in thickness can be readily produced on steel by chemical displacement from buffered solutions of nickel salts. The preferred bath composition and conditions are:

Nickel chloride	600 g.p.l. (80 oz./gal.)
Boric acid	40 g.p.l. (4 oz./gal.)
pH	3.5 to 4.5
Temperature	70°C. (160°F.)
Motion	4.9 meters/min. (16 ft./min.)

2. The immersion deposits can be rendered compact and adherent by subjecting the coated steel to heat treatment at temperatures between 650° and 760°C. (1200° and 1400°F.). This treatment causes diffusion to occur so that the product is really a nickel-iron alloy coating on steel.

3. Thin, heat-treated nickel coatings develop rust in weathering but the

rust that forms is more protective than that on bare steel. If the annealing treatment is prolonged to resemble commercial steel-mill box-annealing, the corrosion rate in outdoor atmospheres is greatly reduced.

4. A long, diffusion anneal is also advantageous when a high iron-nickel alloy surface is desired, as for good adhesion of ceramic enamels.

5. For other uses, a milder heat treatment may be preferable. For example, humidity chamber exposure tests of nickelized-steel panels coated with organic lacquers indicated that a 30-minute heat treatment at 650°C. (1200°F.) yields a superior product.

ACKNOWLEDGEMENT

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Any discussion of this paper will appear in the discussion of section of Volume 94 of the Transactions of the Society.

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THE ELECTROLYTIC PRODUCTION OF ALUMINUM[1]

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ABSTRACT

The development of methods for the electrolytic production of aluminum is discussed. Problems involving heat loss, anode effect, and removal of aluminum from the bath, and modern methods of their solution are described. Construction and operation of the newest type of the Soderberg electrode is detailed and reference is made to the three-layer electrolytic refining process through which very high purity aluminum is obtained.

The electrolytic processes for the production of metals are divided into two classes: those employing aqueous solutions and those requiring the use of fused salts. The latter group are generally much more "touchy" and difficult to operate than the former, largely because of the inherent characteristics of fused salts as such. In the latter group, technical difficulties multiply rapidly as the operating temperatures increase. Bath volatilization and hydrolysis, composition changes due to partial freezing out of high melting constituents of the bath if the temperature drops a little, attack

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on refractory materials, oxidation of the carbon electrodes, and reaction between the deposited metal and the molten bath become increasingly troublesome as the operating temperature is raised. The electrolytic production of aluminum from a fused cryolite bath, carried out at a temperature between 950° and 1000°C., operates at the highest temperature of any of the commercial fused salt processes except the Siemens & Halske process for producing beryllium by the electrolysis of double fluorides. The latter process, however, has only been operated in Germany on a scale which we would hardly class as a large pilot plant operation, and is scarcely likely to have any commercial future in view of competition from other simpler and less expensive processes.

In the light of these facts, it is a significant achievement that both Charles M. Hall and Paul L.-T. Héroult worked out the fundamentals and commercialized the electrolytic production of aluminum in the very early days (before 1890) when dynamos were first becoming available as sources of electric current. The use of a bath of molten cryolite containing dissolved aluminum oxide (the cheapest pure aluminum compound, per pound of aluminum) contained in a carbon-lined steel cathode vessel and electrolyzed with carbon anodes, as developed by these pioneers, is still the basis of the industry. The mechanical developments of sixty years' practical experience with the process have, of course, greatly improved the equipment and technique, but the fundamentals remain the same in spite of many attempts to change or avoid them. Recent industrial developments and operating costs for government plants have been described by Klagsbrun (1).

With the exception of the alkali and alkaline earth metals, any metallic impurities present in the electrolyte, anodes, or alumina are reduced to the metallic form and contaminate the aluminum. In practice, the molten cryolite bath usually contains from 3 to 13 per cent of calcium fluoride, part of which may be added purposely in order to reduce the melting point and part formed from the lime in the ash of the anodes and that present as an impurity in the alumina.

In practice, the current densities, cell voltages, and thermal insulation are so adjusted as to maintain the cell at the proper working temperature. Commercial cells have operated with currents of from 8,000 to 50,000 amperes, voltages from about 4.5 to 7, and current efficiencies of 80 to 90 per cent. A number of such cells have been described in the reports of inspections of the German aluminum plants (2, 3, 4, 5, 6, 7, 8, 9, 10) and the books of Engel, Gregory, and Mossé (11), and Edwards, Frary, and Jeffries (12). A line of 50,000 ampere cells is shown in Fig. 1.

It is obvious that the amount of heat radiated from a large uncovered bath of molten cryolite at approximately 1000°C. would be very great. Artificial covers have been tried but are not successful for a variety of reasons—perhaps chiefly because of the greatly increased oxidation of the anodes when such covers are used. In practice a natural cover is formed by a layer or crust of a mixture of frozen bath and aluminum oxide (which may be from one to three inches thick) on top of the molten bath. This largely reduces the heat losses from the bath surface and, at the same time, hinders the hydrolytic decomposition of the molten bath by the moisture of the air. Aluminum oxide is charged on top of this crust, both for thermal

insulation and in order to preheat it so as to drive off traces of water before it is stirred into the molten bath.

As the electrolysis proceeds, the metal from the aluminum oxide is deposited on the cathodic cell lining and, being slightly heavier than the molten cryolite, remains in the bottom of the cell. The oxygen combines with the anode to form carbon dioxide or carbon monoxide and the energy thus evolved is available for the maintenance of the temperature of the molten bath. When the aluminum oxide content of the bath has dropped to about 2 or 3 per cent, an "anode effect" occurs. The molten bath ceases to wet the carbon anode and becomes separated from the anode surface

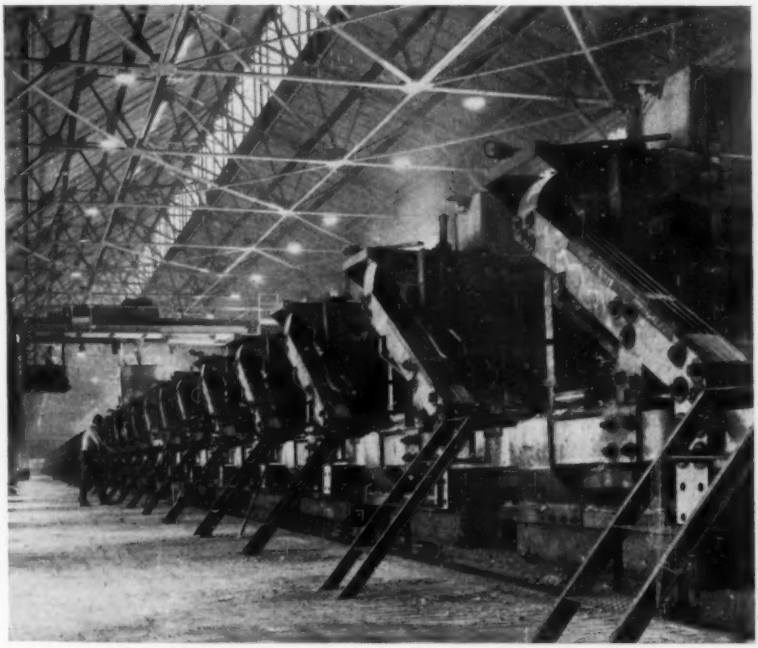

FIG. 1. Part of a line of 50,000 ampere cells, with prebaked anodes, for the production of aluminum.

by a thin film of gas, chiefly carbon monoxide, through which all of the current must pass by means of a multitude of small sparks. Obviously, this requires an increased cell voltage which in practice may rise to 30–60 volts during an anode effect and causes a great increase in heat evolution.

If cells of this type were operated in parallel or in a short series on any kind of generating equipment, this voltage rise would result in severe disturbances. Since a hundred or more such cells are generally operated in series from rectifiers or similar conversion equipment at constant line voltage, this sudden voltage rise of an individual cell only slightly reduces

the current in the circuit and the voltage drop over each of the other cells in the line. In contrast with the constant voltage system used here, some foreign plants use automatic electrical controls to maintain constant current in the line, raising the voltage as necessary when an anode effect occurs. An incandescent signal lamp shunted across the cell terminals glows more or less brightly when the anode effect occurs. By breaking in the crust with heavy steel bars and vigorously stirring in the alumina (and, if necessary, by momentarily short-circuiting the cell), normal voltage and operating conditions can be restored promptly. The alumina dissolved should suffice for from 3 to 8 hours of further operation before the anode effect recurs.

This anode effect is one of the most characteristic and striking phenomena associated with the electrolytic production of aluminum, as well as one of the most important. Although the carbon dioxide gas evolved during normal operation of a cell contains a considerable proportion of carbon monoxide (produced by reaction with the incandescent carbon anode surface or carbon particles floating on the bath, and perhaps partly produced directly in the anode reaction), the carbon monoxide content is greatly increased when the anode effect begins and the amount of carbon dioxide may be reduced nearly to zero. At the same time the proportion of carbon tetrafluoride in the anode gas increases from a small fraction of a per cent to several per cent. The gas is no longer evolved as large bubbles which agitate the molten bath, but is discharged directly to the atmosphere through the annular space between the electrode and the (now quiet) molten bath. The instant the anode effect is destroyed and the voltage drops to normal, the vigorous agitation of the molten bath by large gas bubbles begins again. This description refers particularly to cell having prebaked carbon electrodes, where the phenomena can be easily followed and seen. With Söderberg electrodes, the condition may be somewhat different.

At 1000° C. the density of molten cryolite is just under 2.10, while that of molten aluminum is approximately 2.284 (13). Since the fluorides of calcium, barium, and strontium markedly increase the specific gravity of cryolite, it is evident that the amounts of these substances present must be carefully kept below a point at which the bath would become so dense that the agitation produced in it during normal operation would cause aluminum globules to float and be carried to the anode where they would be oxidized. In practice barium and strontium are present only in traces, and the amount of calcium fluoride is kept below about 15 per cent so as to leave an adequate margin of safety. It is evident that this puts a stringent limitation on the CaO content of the alumina; in practice this should not exceed about 0.04 per cent. Some new cryolite is formed in the bath by the regular addition of aluminum fluoride to neutralize the soda (about 0.6 per cent Na_2O) contained in the alumina employed and there is some mechanical loss of bath due to spillage, absorption in the lining, electrode butts, and carbon raked out of the cell and discarded, etc. In general, the dilution by new cryolite formed or added almost compensates for the calcium fluoride formed from the lime in the alumina and electrode ash. The total consumption of bath materials is reported to be between 4 and 7 pounds per 100 pounds of aluminum (14).

To reduce to a minimum the impurities in the aluminum produced, it is obviously necessary that the carbon anodes have a minimum ash content.[2] In manufacturing them, it is therefore necessary to use calcined petroleum coke or pitch coke instead of foundry coke. The prebaked carbon anodes, which generally have been employed until recently throughout the aluminum industry, may be either round or rectangular in cross section and have varied in size from 4 inch (102 mm.) diameter round rods to a rectangular cross-section of roughly 15 x 50 inches (380 x 1270 mm.). They are supported by suitable copper or aluminum hangers clamped to anode bus bars

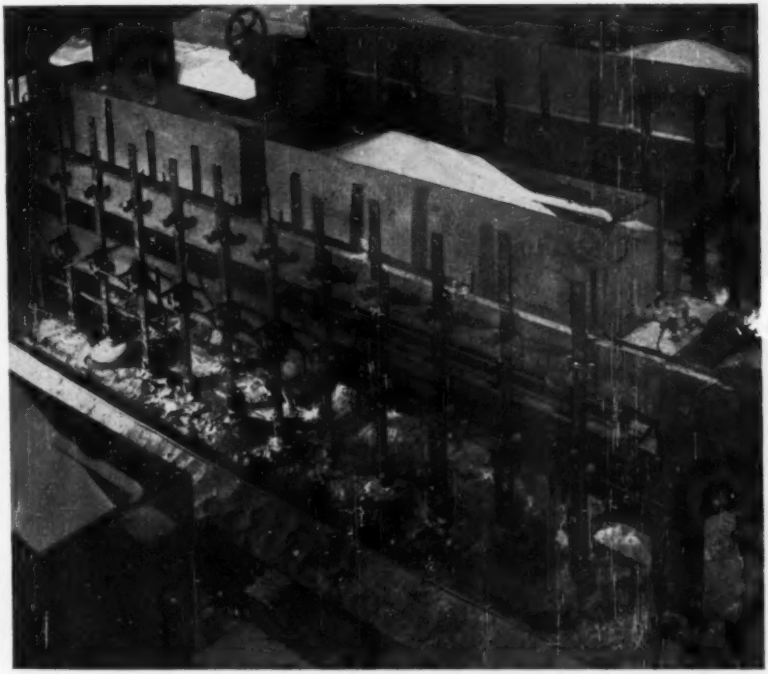

FIG. 2. Top view of cells from line shown in Fig. 1

over the cell, and arranged so as to distribute the current quite uniformly over the whole cross-section of the molten bath and hence over the whole surface of the molten aluminum cathode on the bottom of the cell. Fig. 2 shows electrodes and superstructure of such a cell from the line shown in Fig. 1. Cathode current densities vary considerably in different designs and different sizes of cells, but are generally between 300 and 600 amperes per square foot (0.32–0.65 amp./sq.cm.). Actual anode current densities

[2] The consumption of carbon electrodes is about 60–65 per cent of the weight of aluminum produced.

are more difficult to estimate because the sides of the anodes are active as well as the bottoms, but the longer current path involved produces a lower current density on the sides than on the bottoms of an anode. It is customary to neglect the side areas and figure the density on the basis of the bottom area only. Currents of 5 to 7 amperes per square inch (0.77–1.1 amp./sq.cm.) have been reported on this basis and are probably representative.

After the Söderberg "self-baking" electrode had been developed and shown to be successful for certain types of furnaces, such as those in which calcium carbide is manufactured, attempts were made to introduce it as an anode in the aluminum cells (15). Individual experimental cells were operated by producers both in this country and abroad between 20 and 25 years ago, and the first commercial operation of a full line of aluminum cells with Söderberg anodes began in 1927 at the Alcoa, Tennessee, plant of the Aluminum Company of America. The anodes used here were cylindrical, about 7 ft. (2.1 m.) in diameter and 5 to 6 ft. (1.5–1.8 m.) high, encased in a shell of sheet aluminum and supported by current-carrying clamps attached to a clamping ring. The cells used were circular, of such a size as to give a bath cavity of about 2 ft. (61 cm.) greater in diameter than the anode. They operated on a current of between 25,000 and 30,000 amperes. The bottom end of the anode was baked electrically before the cell was started and then carbon paste[3] (a suitable mixture of petroleum coke, pitch, and tar) was fed into the top of the shell and gradually baked *in situ* by the heat of the cell itself. The anode bottom remained quite flat in operation and the central hole originally provided in the anode for the discharge of gas was found to be unnecessary.

The clamps were cumbersome and unsatisfactory both as a supporting means and as a current-carrying means. They were replaced by other mechanical means of supporting the anode, while slightly conical steel stubs, about 3 inches (76 mm.) in diameter and 2 feet (61 cm.) long, driven into the soft paste through the aluminum shell and subsequently connected to the anode bus with copper flexible cable, served to introduce the current into the anodes. Later, rectangular anodes, supported by a framework of steel channel "logs," were developed and found suitable for use in rectangular cells. The latter are more convenient and economical than circular ones.

Fig. 3 shows a modern cell with this type of electrode. The anode is enclosed within a hood (the door of which has been raised) to carry off the fumes and dust. The two lower rows of stubs are connected by copper straps and flexibles to the anode bus, and the steel channel "logs" are clearly shown. The stubs have been inserted through holes in the logs. This cell had been shut down and the anode raised at the time the picture was taken. Fig. 4 shows the use of a tool for withdrawing the stubs when they have nearly reached the bath level so as to prevent them from coming into contact with the molten bath and dissolving in it. The stubs stick firmly in the baked carbon anode, and the labor required to remove them and drive them into the soft paste again at a higher level is considerable.

In the newest type of Söderberg anode (16, 17), shown in Fig. 5, the con-

[3] The weight of paste consumed is 60–65 per cent of the weight of metal made.

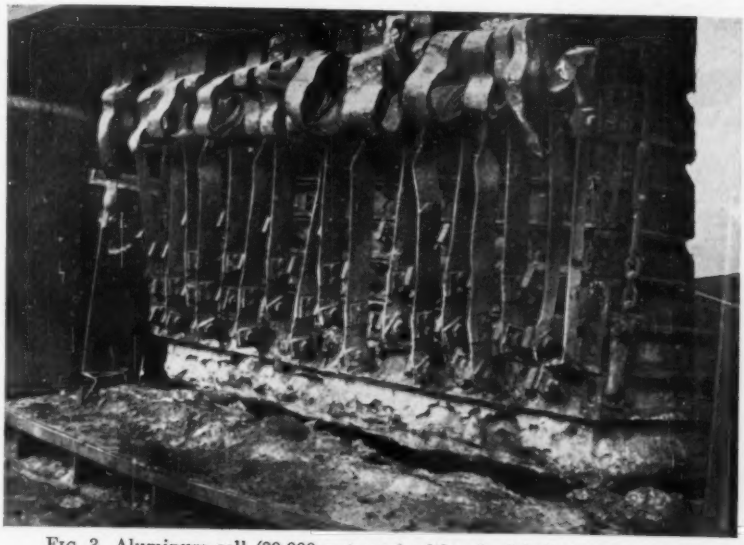

FIG. 3. Aluminum cell (30,000 amperes) with raised Söderberg electrode

FIG. 4. Drawing stub from Söderberg electrode with hand-operated jack

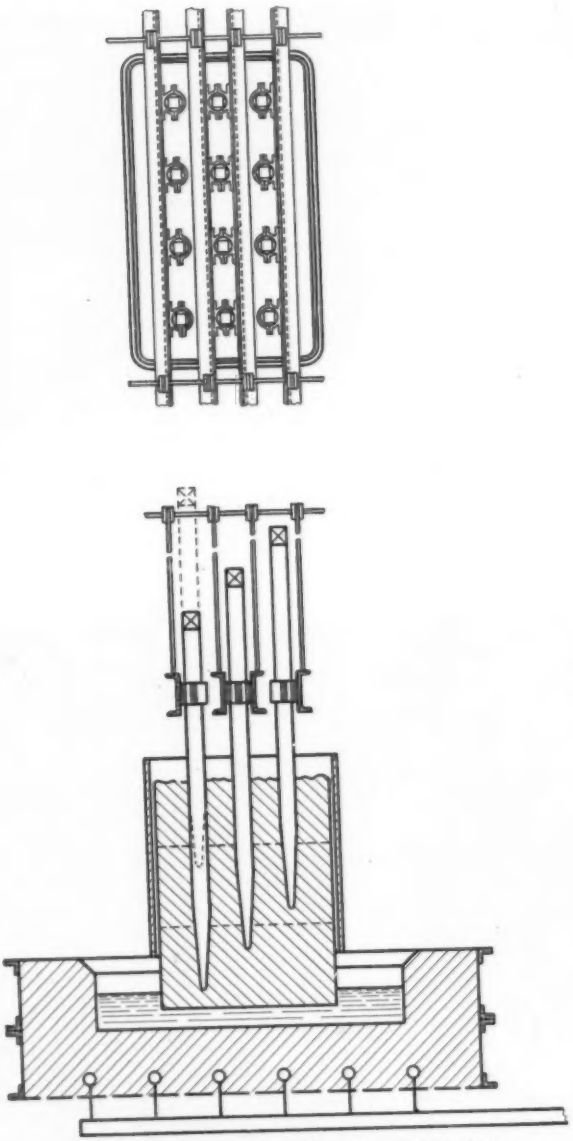

FIG. 5. Söderberg electrode with vertical stubs

struction of the carrying device is simplified and the labor in connection with the anode greatly reduced by the use of vertical instead of horizontal stubs. These vertical steel stubs projecting down through the carbon paste into the baked tip of the anode support its weight and, at the same time, carry the current. They are set at different levels and, at appropriate times, those which extend the farthest into the anode and have come too close to the molten bath are pulled out be a stub-puller carried on a crane. A few pounds of fresh carbon paste are placed in the hole thus left and the stub is driven back again to a position a foot or more above its original position. When the new paste has been baked into a solid mass of carbon by the heat from the cell, the stub is again ready to carry its share of the mechanical and electrical load. While only a limited amount of commercial experience has been had with this type of anode, the results are quite encouraging and the development seems to be a promising one.

Although round cells were used in the original Söderberg anode line mentioned above and have been used with prebaked anodes in a number of foreign plants (2, 10), rectangular cells are preferred for a variety of reasons. Thermal insulation is generally provided by a layer of insulating brick, or the equivalent, between the carbon lining (cathode) and the steel shell. The carbon cathode lining may either be monolithic (made of a mixture of coke, pitch, and tar stamped hot around a suitable form and subsequently baked) or it may be composed of carbon blocks suitably cemented together with carbonaceous paste.

The problem of leading the very large currents (up to 50,000 amperes) from the carbon cathode to the bus, in such a way as to involve a minimum voltage loss between the bus and the metal in the cell, is a serious one. While heavy cast steel sole plates extending over most of the bottom of the cell and supporting the carbon lining were once used extensively, the use of steel collector bars is more common in present practice. These are rectangular or round steel bars extending laterally into the carbon lining and either firmly joined to the steel shell (to which the bus is then attached) or externally connected by copper straps to the cathode bus. They must make good electrical contact with the lining, but must not cause it to crack since the molten aluminum would work down through such cracks and alloy with the steel, thus contaminating the deposited cathode metal.

At suitable intervals (e.g., every second or third day) the molten metal which has been deposited must be removed from the electrolytic cell. Formerly this was accomplished by tapping (the tap hole being subsequently closed with a wooden plug) or by sinking a cast iron or carbon ring into the bath and metal, ladling out the bath from inside the ring and then ladling out the metal which rose in the ring under the influence of the hydrostatic head of the molten bath. More modern methods of metal removal include siphoning (18) or pumping (19) the molten metal into a suitable crucible from which it can be poured into pigs. In some of the German plants the metal was removed by a vacuum suction equipment which drew it out of the cell and into a closed refractory-lined barrel-shaped container from which it could be tapped into pigs (20, 21).

Improvements in the purity of the alumina and the carbon anodes, and in the technique of electrolysis, have resulted in steady increases in the purity of the aluminum produced. With suitable precautions, consider-

able quantities of metal with a purity greater than 99.8 per cent can regularly be produced in the electrolytic cells. To produce the higher purities which may be required for special purposes, the 3-layer electrolytic refining process (which was first operated practically in the Hoopes cell) (22) has been operated both here and abroad. Several foreign installations of this type have been described (17, 21, 23, 24, 25, 26), particularly the German installations in which impure scrap aluminum was refined during the war.

In essence, the process consists in increasing the specific gravity of the cryolite bath (by the addition of barium and calcium salts) to about 2.8, so that pure aluminum will float upon the surface of the bath, and using as anode (beneath the molten bath layer) an aluminum-copper alloy containing enough copper to make it considerably heavier than the bath. Aluminum is electrolytically dissolved from the molten anode and deposited upon the floating molten pure aluminum cathode. From time to time, refined metal is removed from the cathode and additional commercial aluminum added to the anode alloy. Considerable tonnages of metal having a purity of over 99.99 per cent have been made by this process both here and abroad.

The steadily increasing demand for aluminum and the sharpness of its competition with other metals have emphasized the necessity of improvements which will reduce costs and selling prices. Much of the modern market demand is for alloys which have to be made of aluminum of a purity commercially rare or unavailable twenty-five years ago. This puts increasing pressure on the development of improved techniques of producing and handling the metal, and demands a higher quality of raw materials. Active developments in reducing costs and improving purity of product are going on all over the world in this young and vigorous metal industry, and will steadily improve the competitive position of aluminum in modern metals technology.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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